

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No. : **10/585,215**  
Filed/371(c) : June 30, 2005  
Applicant : Ansgar Werner, et al.  
Title : USE OF A METAL COMPLEX AS AN N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTING MATERIAL AND ELECTRONIC COMPONENT, AND ALSO A DOPANT AND LIGAND AND PROCESS FOR PRODUCING SAME  
  
Confirmation No. : 9620  
Art Unit : 2815  
Examiner : Anthony Ho  
  
Attorney Docket No. : 17346-0088  
Customer No. : 29052

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**REQUEST FOR RECONSIDERATION OF PETITION UNDER 37 C.F.R. § 1.47(a)**

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Via EFS-Web  
Commissioner for Patents  
Alexandria, VA 22313-1450

Sir:

Responsive to the Petition Decision mailed December 16, 2010 ("Decision 2"), the Applicants respectfully request reconsideration of the petition under 37 C.F.R. § 1.47(a) to make the above-referenced application on behalf of an inventor who cannot be contacted because he avoids or refuses all of the Applicants' communications, thereby demonstrating his refusal to accept and sign the necessary documents.

**I. Summary**

This petition is being submitted because inventor Olaf Kühl refused to accept and sign the necessary paperwork after a diligent effort to contact and deliver the papers to him. Therefore, inventors Ansgar Werner, Simon Gessler, Horst Hartmann, Andre Grüssing, Michael

Limmert, Andrea Lux, and Kentaro Harada, request that the application be made on their own behalf and on behalf of the non-signing joint inventor, Olaf Kühl.

A petition under 37 C.F.R. § 1.47(a) requires the following:

- (1) the petition fee;
- (2) a statement of the last known address of the non-signing joint inventor;
- (3) factual proof that the missing joint inventor refuses to sign and/or cannot be located or reached; and
- (4) an oath or declaration executed by the signing joint inventors on their behalf and on behalf of the non-signing joint inventor.

Each of these required items has been submitted, either previously or herewith, and a detailed description of each item is offered in the following sections.

## **II. Item (2)**

As Olaf Kühl has relocated since the filing date of the first petition, the Applicants have made a diligent effort to contact him at three addresses. Therefore, the Applicants have satisfied the recommendation that “other addresses at which the nonsigning inventor may be reached should also be given.” M.P.E.P. § 409.03(e).

### *i. Previous Last Known Address*

In the original petition of February 24, 2009 (“Petition 1”), the Applicants stated that “the last known residential address of joint inventor Olaf Kühl is Mittelstrasse 10, 04416 Markkleeberg, Germany.” (Petition 1, p. 2).

The Attorney Advisor accepted this statement in the Petition Decision that mailed August 30, 2010 (“Decision 1”), and noted that the “Applicants completed” this requirement with the

“subject petition.” (Decision 1, p. 2).

Since the filing of Petition 1 and the mailing of Decision 1, however, the address of Olaf Kühl has changed. Therefore, the Applicants submit herewith a statement of two last known addresses.

*ii. Last Known Work Address*

Olaf Kühl’s last known work/office address is the following:

Dr. Olaf Kühl  
Institut für Biochemie  
Felix-Hausdorff-Strasse 4  
17487 Greifswal  
Tel.: +49 (0)3834 86-4320

This address is shown in Exhibit 1, which includes a printout and screenshots of the University of Greifswald’s webpages that list Olaf Kühl. The second page of Exhibit 1 lists Olaf Kühl under the heading “Guest scientists and Postdocs.” This fact is discussed further under section III. Section III also describes the Applicants’ diligent attempt to contact Olaf Kühl at this address.

*iii. Last Known Residential Address*

The last known residential address of Olaf Kühl is the following:

Dr. Olaf Kühl  
Wollweberstrasse 10  
17489 Greifswald  
Tel.: 03834 51 95 49

This address is shown in Exhibit 2, which is a screenshot of a German online telephone directory that shows the address of Olaf Kühl. Exhibit 2 also shows in the first tab an email search that produced Olaf Kühl’s email address: olaf.kuhl@gmail.com. Section III describes the Applicants’ diligent attempt to contact Olaf Kühl at his private mailing address and email

address.

**III. Item (3)**

This section describes the Applicants' diligent attempts to contact Olaf Kühl at the previously-described mailing addresses, email addresses, and telephone numbers. Also described is Olaf Kühl's refusal to accept and sign any of the pertinent documents.

*i. Previously Submitted Evidence*

The Applicants previously submitted the evidence described in this subsection in Petition 1 and the Petition filed November 1, 2010 ("Petition 2"). Nevertheless, the Applicants include it in the present petition because the evidence demonstrates the Applicants' ongoing diligent efforts to contact Olaf Kühl. The Applicants also present new evidence as part of the present petition.

The attached letter (Exhibit 3) from Dr. Volker Scholz describes, in part, the diligent effort to contact the non-signing inventor, Olaf Kühl. The German mailing labels (Exhibit 4) corroborate these efforts. The Applicants offer the following translations to assist in the understanding of the accompanying German mailing labels:

- (a) "nicht angetroffen" – "not found" (top half of page 1)
- (b) "Übergabe-Einschreiben mit Rückschein" – Germany's version of "Certified Mail," *i.e.* requires the signature of the recipient (top half of page 2); and
- (c) "Empfänger benachrichtigt" – "addressee informed" (top and bottom half of page 2).

The Applicants respectfully submit that the letter from Dr. Scholz and the copies of the mailing labels reflect a *bona fide* and diligent effort to contact the non-signing inventor, Olaf Kühl, at his previous last known address.

*ii. New Evidence*

Since the mailing of Decision 2 on December 16, 2011, the Applicants have continued their diligent effort to contact Olaf Kühl while collecting the required evidence.

*a. Affidavit of Manuela Krumbiegel (“Affidavit”)(Exhibit 5)*

The first new evidence is the affidavit of Manuela Krumbiegel, an employee of the assignee of the present application, Novaled AG. Krumbiegel, as described in the affidavit, is responsible for managing the inventions of Novaled AG’s employees. The affidavit was notarized by Dr. Joachim Püls, and serves as a “statement of facts,” which is recommended by sections 409.03(d) I. and II. of the M.P.E.P.

Specifically, “a statement of facts should be submitted that fully describes the exact facts which are relied on to establish that a diligent effort was made” to contact the wayward inventor. M.P.E.P. § 409.03(d) I. Also, “[w]here a refusal of the inventor to sign the application papers is alleged, the circumstances of the presentation of the application papers and of the refusal must be specified in a statement of facts by the person who presented the inventor with the application papers and/or to whom the refusal was made.” M.P.E.P. § 409.03(d) II. Krumbiegel’s affidavit serves this purpose.

Paragraph 3 of the affidavit is a statement that supports the efforts previously described in section III. i. Krumbiegel sent the documents to Olaf Kühl’s private address on December 12, 2008 by registered mail “because Dr. Olaf Kühl had already refused to sign the documents before.” (Affidavit, p. 1). Olaf Kühl did not respond to the notice left in his mailbox, nor did the post office present Krumbiegel with any indication that the

package had been improperly addressed. Due to Olaf Kühl's failure to accept or pick-up the package, it was returned "un-delivered." (*Id.*).

The remaining paragraphs of the Affidavit further explain the additional and diligent efforts to contact Olaf Kühl, as corroborated by the following new pieces of evidence:

*b. Letter to Olaf Kühl's Last Known Work Address (Exhibit 6)*

Exhibit 6 is a copy of the cover letter and attachments sent by Krumbiegel to Olaf Kühl's last known work address, which is described in section II. ii. An English translation of the letter also is provided. The cover letter informed Olaf Kühl of his refusal to accept the previous package, and asked him to sign the pertinent documents. The documents attached to the letter included the assignment, declaration, and text of the application.

These attachments along with the cover letter were delivered by the United Parcel Service ("UPS") to Olaf Kühl's address at the University of Greifswald on April 4, 2011. This delivery date is shown in Exhibit 7, which is a copy of the original UPS delivery receipt. Exhibit 7 also includes an English translation of the receipt. The delivered package, according to Exhibit 7 and the Affidavit, was received by "Mr(s). Groth" at the University of Griefswald. (Affadavit, p. 1).

*c. Telephone Call to the University of Greifswald*

Despite the package's confirmed delivery, Olaf Kühl did not respond on or before April 21, 2011. On that day, Krumbiegel contacted the University of Greifswald to determine whether Olaf Kühl received the cover letter and attachments. As sworn in

paragraph 5 of the Affidavit, Krumbiegel spoke with Christina Voss, “who is secretary of the Mathematics-Science Faculty” at the University of Greifswald. (Affidavit, p. 2).

When asked if Olaf Kühl received the package, Voss told Krumbiegel that “Olaf Kühl was only employed until 31<sup>st</sup> of March 2011 but is still coming occasionally to work there and should have received the letter.” (*Id.*)(emphasis added).

*d. Telephone Call to Olaf Kühl's Private Residence*

Due to the uncertainty presented by Olaf Kühl’s employment status as a “guest scientist,” Krumbiegel telephoned his private residence on April 24, 2011. Olaf Kühl’s wife answered the phone, and, as sworn in paragraph 6 of the Affidavit, told Krumbiegel to “send the documents to [Olaf Kühl’s] private address.” (Affidavit, p. 2). In order to do so, Krumbiegel confirmed with Mrs. Kühl the accuracy of the address to which she mailed the documents. (*Id.*) This address is described in section II. iii.

*e. Letter to Olaf Kühl's Private Address (Exhibit 8)*

A copy of the cover letter mailed to Olaf Kühl’s private address is shown in Exhibit 8. Exhibit 8 also includes an English translation of the cover letter. The cover letter’s attachments were the same as those in Exhibit 6.

The cover letter of Exhibit 8 explained the previous efforts to contact Olaf Kühl, and asked him to inform Krumbiegel if he did not intend to sign the pertinent documents. Also, please note that the date on the cover letter in Exhibit 8 is incorrect. The letter was sent April 24, 2011, instead of May 24, 2011, because Krumbiegel swears in paragraph 7 of the Affidavit that she sent it “on the same day” that she telephoned Olaf Kühl’s private residence.

Paragraph 7 of the Affidavit also states that Krumbiegel received a notice from UPS on April 26, 2011, just two days after sending the cover letter. A copy of this notice is shown in Exhibit 9. The notice states that “THE RECEIVER DID NOT WANT THE ORDER AND REFUSED THIS DELIVERY.” (Exhibit 8, p. 1). As a result, UPS returned the letter to Novaled AG.

The Applicants respectfully submit that Olaf Kühl’s refusal of the package is sufficient to demonstrate his refusal to sign or join the application, because section 409.03(d) II. of the M.P.E.P. states that “[p]roof that a *bona fide* attempt was made to present a copy of the application papers...to the nonsigning inventor for signature, but the inventor refused to accept delivery of the papers or expressly stated that the application papers should not be sent may be sufficient” to show a refusal to join.

*f. Emails to Olaf Kühl*

After receiving the refusal notice from UPS, Krumbiegel searched the internet for Olaf Kühl’s email address. Her search produced two addresses: oevel@yahoo.com, and olaf.kuhl@gmail.com. Krumbiegel sent a message to the first address and carbon copied the second. A copy of this email is shown in Exhibit 10. Exhibit 10 also includes an English translation of the email.

The email explained the notice from UPS, and asked Olaf Kühl if he was, in fact, refusing to sign the documents. Krumbiegel also informed Olaf Kühl in the email that she would forward the documents to him yet again if he wished to sign them.

Olaf Kühl did not respond to the email, as sworn in paragraph 8 of the affidavit.

*iii. Summary*

When confronted by the Applicants' above-described diligent efforts, Olaf Kühl, either avoids contact or refuses to accept delivery of the documents that must be signed. After attempting to contact Olaf Kühl at his private address, work address, private telephone number, work telephone number, and two email addresses, the Applicants respectfully submit that they have exhausted all reasonable avenues of communication.

For this reason, Olaf Kühl cannot be contacted, because he neglects all of the Applicants' communications. The Applicants also submit that the appended evidence demonstrates Olaf Kühl's refusal to accept and sign the documents pertaining to the present application. In other words, he refuses to join the application.

The Applicants submit that this fact has been demonstrated by the appended statement of facts and the relevant evidence.

**IV. Item (4)**

Decision 2 also states that the Applicants have not satisfied item (4) because the "applicants submitted a declaration signed by co-inventor Kentaro HARADA," but "[t]he above-captioned application has eight inventors." (Decision 2, p. 3).

Harada and the remaining inventors, with the exception of Olaf Kühl, signed the original declaration. As a result, Harada was and is aware of the application's inventorship. The Applicants, therefore, respectfully submit that the second declaration was proper.

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Filing/371(c): June 30, 2005  
Petition Under 37 C.F.R. § 1.47(a)

Since the Applicants previously submitted the petition fee, no additional petition fees are believed due at this time. The Commissioner is authorized, however, to charge the extension of time fee and any other necessary fees to Deposit Account No. 19-5029.

Respectfully submitted,

  
\_\_\_\_\_  
Joshua B. Aronson  
Reg. No. 64,504

**Date: June 16, 2011**

SUTHERLAND ASBILL & BRENNAN LLP  
999 Peachtree Street, NE  
Atlanta, GA 30309  
Telephone: 404-853-8000  
Facsimile: 404-853-8806

**Attorney Docket No.: 17346-0088**

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# Exhibit 1

Internet search 20th January 2011 gave the following results:

1) work place



<http://www.uni-greifswald.de/index.php?id=14541>

PD Dr. Olaf Kühl  
Institut für Biochemie

Felix-Hausdorff-Straße 4, 17487 Greifswal  
Tel.: +49 (0)3834 86-4320  
[oevel@yahoo.com](mailto:oevel@yahoo.com)

Privatdozent Dr. Olaf Kühl wurde in diesem Jahr zum „Celebratory Most Cited Dinner“ der Royal Society of Chemistry nach Washington DC eingeladen. Mit dieser Einladung werden jedes Jahr die Autoren der 50 am häufigsten zitierten Beiträge in den beiden Prestige trächtigsten Zeitschriften der *Royal Society of Chemistry*, *Chemical Communications* und *Chemical Society Reviews* ausgezeichnet. Die Zeitschriften veröffentlichen zusammen jährlich etwa 1.900 Beiträge.

Dr. Olaf Kühl arbeitet auf dem Gebiet der (bio)chemischen Katalyse. In der Katalysechemie werden (bio)chemische Reaktionen entwickelt, die das gewünschte Produkt mit einem geringeren Einsatz von Ressourcen vorzugsweise in besserer Qualität liefern. Hierbei werden im allgemeinen dadurch Kosten gespart, dass weniger Energie verbraucht wird, weniger Lösungsmittel in die Umwelt gelangen und weniger Abfallstoffe erzeugt werden.

Katalytische Reaktionen bilden nicht nur die Grundlage vieler moderner großtechnischer Verfahren in der Chemie, sondern auch der physiologischen, also chemischen Reaktionen innerhalb von Lebewesen (vom Einzeller bis zum Menschen). Hierbei werden die katalytischen Reaktionen zumeist von Enzymen, speziellen körpereigenen Proteinen, durchgeführt. Mithilfe dieser Enzyme ist der Körper in der Lage, eine Vielzahl unterschiedlicher Prozesse störungsfrei ablaufen zu lassen, während der Chemiker diese Prozesse stofflich und räumlich voneinander trennen muss.

Dr. Kühl beschäftigt sich sowohl mit der chemischen als auch mit der biochemischen Katalyse und hier besonders mit metallhaltigen Enzymen. So war er kürzlich maßgeblich an der Aufklärung der Funktionsweise mehrerer metallhaltiger Enzyme beteiligt und hat dafür Konzepte der anorganischen Chemie erfolgreich in die Biochemie integriert.

Ein weiterer Schwerpunkt seiner Forschung ist die Entwicklung neuer Moleküle, sogenannte Liganden, die an Metalle binden und mit ihnen ein Katalysatormolekül bilden. Die Eigenschaften dieser Liganden lassen sich durch Einführung spezieller, funktioneller Gruppen gezielt verändern. Dadurch können die Katalysatoren den jeweiligen Anforderungen angepasst werden, um großtechnische Prozesse optimieren zu können.

Doktor - Universität Greifswald • Mozilla Firefox

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Naturwissenschaften

Medizin

Hochschule für Technik

ausgezeichnete Universität

Gütesiegel Qualitätssicherung

Internationalisierung

Wissenschaftliches

Sekretariat



**Olaf Kohl**

Dinner für Zitate

Personalprofil Dr. Olaf Kohl wurde in diesem Jahr vom „Laboratory Head Council“ der Royal Society of Chemistry nach Würdigung seines herausragenden Beitrag zu einer besseren Verständigung zwischen Chemikern und Nicht-Chemikern als „Young Chemist of the Year“ ausgezeichnet. Die Zeitschrift hat veröffentlicht, dass Dr. Kohl mit seinem Projekt „Dinner für Zitate“ auf dem Gebiet der Bioverarbeitung Chemie und Biologie verbindet, die den gemeinsamen Produkten herkömmlicher Enzyme und Katalysatoren vergleichbar sind. Beide werden von Organismen produziert, um weniger Energie verbraucht wird, welche Lebensmittel in die Umwelt entlassen und weniger Abfallstoffe erzeugen.

Chemische Reaktionen führen nicht nur die Grundlagen vieler medizinischer, technologischer und industrieller Prozesse, sondern auch die Basis für viele ökologische Anwendungen aus (z.B. Wasser- und Bodenreinigung, Abfallbehandlung). Nachdem vorher die Anwendung von Enzymen, zumeist aus tierischen Präparaten, ausgeschlagen, wurde diese Entwicklung in den letzten Jahren ein Vorbild unterschiedlichster Prozesse stellvertretend abgebaut zu lassen, indem der Chancen der Prozesse möglichst vollständig und vielseitig ausgenutzt wurden.

Dr. Kohl beschäftigt sich sowohl mit der chemischen wie auch mit der biologischen Katalyse und hat besonders mit metallhaltigen Enzymen. So war er für die Entwicklung eines von mir entwickelten Prozesses wesentlich verantwortlich, der Enzyme benötigt und hat dafür einen der am weitesten breiten Anwendungsbereichen der Chancen der Prozesse möglichst vollständig und vielseitig ausgenutzt.

Ein weiterer Schwerpunkt seiner Forschung ist die Entwicklung neuer Methoden, um organische Lipide zu analysieren und mit ihnen eine Katalysatormarkierung zu erhalten. Die Informationen dieser Lipide lassen sich durch Katalysatoren spezifisch.

PD Dr. Olaf Kohl | Posteingang: M | Dr. Kohl teilt an | Dr. Kohl - Uni... | 32/29

Guest scientists and earlier coworkers – Mozilla Firefox

Geöffnete Seiten: 3 | Geschichte: Opera - Lesbenchen - Parrot - Hilla

http://www.uni-greifswald.de/~chemistry-anorg/scientists.htm

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Guest scientists and coworkers



Institut für Anorganische  
Ernst-Moritz-Arndt-Universität Greifswald  
**Inorganic Chemistry**

Welcome to the Hirschfeld group

### Guest scientists and coworkers

#### Guest scientists and Friends

- ✉ PD Dr. Olaf Kohl
- ✉ Prof. Dr. Tamás Vértesy (Budapest)
- ✉ Prof. Dr. László Nyíregyháza (Budapest)
- ✉ Prof. Dr. Cun-Yue Guo
- ✉ Prof. Dr. Raj K. Bental (Israel)
- ✉ Prof. Dr. Abu Mawgoud
- ✉ Prof. Dr. Eugenius Nortus (Vilnius)

- ✉ Dr. Norman Peuckert
- ✉ Dr. Dmitry Yakovlev
- ✉ Dr. Andrej Karšišek (Kroatien)
- ✉ Dr. Weijia Peltman Gora
- ✉ Dr. Mostafa Abd-E-Malek
- ✉ Dr. Dilek Berkoual
- ✉ Dr. Elvira Matraca
- ✉ Dr. Anushka Surendra
- ✉ Dr. Deepesh C. Sharma
- ✉ Dr. Pandu Sengariva
- ✉ Dr. Neelima Gupta (Japan)

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# Exhibit 2

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## 2) Privat adress

Wollweberstr. 10  
 17489 Greifswald  
 Tel 03834 51 95 49  
Olaf.kuhl@gmail.com

**Das Telefonbuch Deutschland - Online Telefonauskunft - Telefonkennbuch - Telefonbuch online - Telefonkartei - Telefonkartei online**

Olaf Kuhl - Adressen - Orte - Ortebuch - Suchbegriffe - Extras - Hilfe

http://www2.dastelefonbuch.de/rm-detail?recuid=PVCXH4XJ4HYCLARWLTZ3S1P2GCP0256V5A4YCB0=1&ap=69&aktion=

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Suche nach: [ ]

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**Kühl, Olaf**

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**Das Telefonbuch**

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**Das Telefonbuch**

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# Exhibit 3

# BOEHMERT & BOEHMERT ANWALTSSOZIETÄT

RECEIVED  
MAY 22 2019

BOEHMERT & BOEHMEXT Meissnerstraße 26 10719 Berlin

BY DHL-COURIER

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Baker Botts L.L.P.

Attn: Mr. Gary M. Butter

Mr. Gary M. B.

30 ROCKAWAY  
3341-FL

44th Floor  
N. Mail NM 10110 3000

New

USA

|                                                                    |                                                           |
|--------------------------------------------------------------------|-----------------------------------------------------------|
| HILDE KARL BÖHMERT (1909-1931)                                     | PROF. DR. WILHELM NORDENKAMPF AL PERINUS                  |
| DIPLO.-ING. ALBERT BÖHMERT (1907-1961)                             | DIPLO.-PHYS. EDGARD BAUMANN H. HOMMENHOFER                |
| WILHELM H. BEAUMER (1913-1988)                                     | DR. DR. HEROLD KLÖSTNER V. SPORNHAUER                     |
| DIPLO.-ING. WALTER BÖHMANN (1911-1988)                             | DIPLO.-ING. HANS W. GRÖNING H. M. WERNER                  |
| PROF. DR. HEINZ GODDARZI (1905-1988) <i>Wissenschaftler</i>        | DIPLO.-ING. SIEGMUND SCHIRMER H. R. SPÄTH                 |
| DIPLO.-ING. ROLAND HÜNGGARI (1913-1988) <i>Wissenschaftler</i>     | DR. DR. ERNST HÄNEMANN H. V. STÖCKLER                     |
| WOLFGANG KUNZ (1913-1988) <i>Wissenschaftler</i>                   | DIPLO.-ING. ARTHUR PFEIFFER BREDIGER V. PAUL PAT. WILHELM |
| DR. LUDVÍK KOUTNER (1913-1988) <i>Wissenschaftler</i>              | SIEGL-CHAM. DR. DIETER LAUDER H. V. WILHELM               |
| DR. (CHARLES) ANDRAS WINKLER (1913-1988)                           | CHRISTOPH SCHÖMELD V. SPORNHAUER                          |
| MICHAELA RUTH-DITTRICH (1913-1988)                                 | DR. JEN. DIPLO.-ING. JAN LÖHNING H. V. SPORNHAUER         |
| DIPLO.-PHYS. DR. MARION TÖRNHARDT (1913-1988)                      | DIPLO.-PHYS. CHRISTIAN REINHOLD H. V. SPORNHAUER          |
| DR. ANTONIA WERTH-WEISBERGER (1913-1988)                           | DR. ANKE NORDENKAMPF-BECKHARDT H. V. SPORNHAUER           |
| DIPLO.-ING. IVA LEBERGACO (1913-1988)                              | MALTE HINTZIG, LL.M., H. V. SPORNHAUER                    |
| PROF. DR. ALEX HÖRMANN (1913-1988)                                 | DIPLO.-PHYS. ANDREAS ZOLEWARTH-ROCHFORD H. V. SPORNHAUER  |
| DIPLO.-PHYS. DR. CORNELIA WEBER-KRÜSL (1913-1988)                  | DR. KATHARINA KRÖTZ H. V. SPORNHAUER                      |
| DIPLO.-PHYS. DR. STEFAN SCHÖRE (1913-1988)                         | DIPLO.-KIOS. DR. ILKA PREIBISCH H. V. SPORNHAUER          |
| DR. IMMO MATTHIAS PFEIFFER (1913-1988)                             | DR. RUDOLF BÖCKHNAHL H. V. SPORNHAUER                     |
| DR. MARTIN WITZL (1913-1988)                                       | DR. THOMAS W. BODDIN H. V. SPORNHAUER                     |
| PROF. DR. JAH BRUNO NORDENKAMPF (1913-1988)                        | DIPLO.-ING. DR. MAGDALENE LÖBLERBACH H. V. SPORNHAUER     |
| DR. CHRISTIAN CZYCHOWSKI (1913-1988)                               | DIPLO.-BLOCKHELD DR. GUNHILD J. HUPPE H. V. SPORNHAUER    |
| DR. CARL-RICHARD HAASMARK (1913-1988)                              | DIPLO.-SICHTER DR. KATHARINA M. GRÄFEL H. V. SPORNHAUER   |
| DIPLO.-PHYS. DR. INGO JÜRGEN HÄNSCHEN (1913-1988)                  | CHEMIEBLEI-PFLEISTER AL. SPORNHAUER                       |
| DIPLO.-PHYS. DR. THOMAS E. REINHOLD (1913-1988)                    | DR. KURTAT WAGNER H. V. SPORNHAUER                        |
| DR. VOLKER SCHMITZ-FOHRINGER (1913-1988)                           | DIPLO.-PHYS. DR. XIA SPAŁA-KRZYZEK H. V. SPORNHAUER       |
| DIPLO.-ING. DR. JAKOB SEKORA (1913-1988)                           | DIPLO.-PHYS. DR. ULRICH GÖTTSCHE H. V. SPORNHAUER         |
| DIPLO.-PHYSIKER DR. GERMAR REINHOLD H. V. SPORNHAUER               | DR. FRANCIS BRODNERA H. V. SPORNHAUER                     |
| DIPLO.-CHEM. DR. KAREL HEINZ B. KITTNER (1913-1988)                |                                                           |
| DIPLO.-ING. JULIA T. F. SCHÖNIG (1913-1988) <i>Wissenschaftler</i> |                                                           |
| DR. FLORIAN SCHNAID (1913-1988) <i>Wissenschaftler</i>             |                                                           |
| DR. ANDREAS DÜTSCHMANN (1913-1988)                                 |                                                           |
| DR. VOLKER SCHAFER (1913-1988)                                     |                                                           |
| DR. MARTIN SCHÄFER (1913-1988)                                     |                                                           |
| DIPLO.-PHYS. DR. MICHAEL RÄSTY (1913-1988)                         |                                                           |
| DIPLO.-PHYS. DR. STEFFEN SCHMIDT (1913-1988)                       |                                                           |
| DR. ANDRÁS LUCZ (1913-1988)                                        |                                                           |

Ihr Zeichen/Your ref.  
071956.0113

### Ihr Schreiben/Your letter

Unse Zeichen/Our ref.  
**N60056US**

Berlin,  
February 20, 2009

USA - Patent Application 10/585,215 - Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same - Novaled GmbH

Dear Mr. Butter,

Referring to your letter of October 8, 2008. Please find enclosed the combined Declaration and Power of Attorney signed by all inventors except of Olaf Kühl. With regard to the inventor Olaf Kühl the applicant has attempted to send the inventor the declaration by a method which requires the inventor to sign (certified mail - "Übergabe-Einschreiben mit Rück-schein") it was tried twice to deliver the declaration to the inventor at Mittelstrasse 10, 04416 Markkleeberg, the place of residence of Mr. Kühl. Mr. Kühl did not open. Therefore, he was informed by the postal office to fetch the letter. This can be taken from page 2, upper part, the box "Empfänger benachrichtigt" (addressee informed) dated January 7, 2009. Mr. Kühl did not appear at the postal office to take the respective letter of the applicant. Now, the legal term for keeping such letters has lapsed and the letter was re-sent to our applicant. Thus, it is our understanding, that all due care was taken by the applicant to send the declaration to Mr.

MÜNCHEN    BERLIN    BONN    DÜSSELDORF    FRANKFURT    HAMBURG    POTSDAM    KIEL    MÖRNICKIRCHEN    ALICANTE    PARIS    SHANGHAI  
Meinekestraße 26    D-10719 Berlin    Telefon +49-30-23607070    Telefax +49-30-236076721  
www.boehmert.de    V.Schub@boehmert.de

BOEHMERT & BOEHMERT

- 2 -

Kühl, but he ignored it. As already informed, the relation between the patentee and Mr. Kühl might be somewhat better.

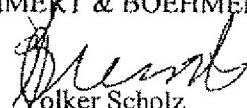
Please let us know whether such document is sufficient to proof that the inventor was sent the declaration and refused to sign it. It is our understanding that the applicant may not provide any better proof in this regard.

If you deem the documentation sufficient, please forward it to the USPTO.

For any further questions, please let us know.

Best regards,

Very truly yours  
BOEHMERT & BOEHMERT



Volker Scholz

Enclosure:

Combined Declaration and Power of Attorney  
Documentation with regard to inventor Olaf Kühl

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**4**

# **Exhibit 4**

4097

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Nr. EC 480313



Lagerfrist überschritten  
Zurück an Absender  
 Entwurf - EG  
 Übergabe-EG, Rückschein  
 Übergabe-EG, eigenhändig  
 Übergabe-EG, Rückschein, eigenhändig

## Ihr Briefdienst für Sachsen

[www.post-modern.de](http://www.post-modern.de)

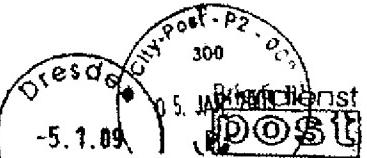
Novaled AG · Tatzberg 49 · 01307 Dresden

Herr Dr. Olaf Kühl

Mittelstrasse 10  
D-04416 Markkleeberg

Frist abgelaufen

- i / / / /
- EINWURF  
EINSCHREIBEN
  - Rückschein (EE)



Unzustellbar

10.01.09 K6

- Nicht angetroffen
- Kein Briefkasten vorhanden
- Briefkasten überfüllt
- Annahme verweigert
- Anschrift unvollständig/falsch
- Verstorben/Firma erloschen
- Empfänger unbekannt
- Empfänger verzogen nach

Str.: Zwei Zentrale

PLZ/Ort: 950 und 1030

UDBACT geprüft:

|                                                                                                                                                                                           |  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| <b>Rückschein</b>                                                                                                                                                                         |  |
| <input type="checkbox"/> Entwurf - EG<br><input type="checkbox"/> Übergabe-EG, Rückschein<br><input type="checkbox"/> Übergabe-EG, eigenhändig                                            |  |
| <b>Absender</b><br>Name: <i>DR. O. KÜHL</i><br>Adresse: <i>MITTTELSTR. 10</i><br>PLZ/Ort: <i>04416 MARKKLEEBERG</i><br>Telefon: <i>030/247759</i><br>E-Mail: <i>OLAF.KUEHL@NOVALED.DE</i> |  |
| <b>Empfänger</b><br>Name: <i>HERR DR. O. KÜHL</i><br>Adresse: <i>MITTTELSTR. 10</i><br>PLZ/Ort: <i>04416 MARKKLEEBERG</i>                                                                 |  |
| <b>Frachtarten</b><br><input type="checkbox"/> Paket <input type="checkbox"/> Brief <input type="checkbox"/> Zeitung <input type="checkbox"/> Zeitungspaket                               |  |
| <b>Warenbeschreibung</b><br><input type="checkbox"/> empfängt <input type="checkbox"/> abgibt <input type="checkbox"/> keine Warenbeschreibung                                            |  |
| <b>Haftungserklärung</b><br>Ich habe die Sendung dem Empfänger sicher und ordnungsgemäß übergeben.<br>Datum: <i>10.01.09</i> Uhrzeit: <i>10:00</i>                                        |  |
| <b>Zusätzliche Unterschrift</b><br><i>X</i>                                                                                                                                               |  |

postModern Service Telefon: 0800 - 99 99 33 1



**Zustell- und Empfangsbestätigung  
Einschreiben**

NovaledAG Tarifbegleiter 03901 Dresden



Ihr Postdienstleister

- Einwurf-Einschreiben
- Übergabe-Einschreiben  eigenhändig
- Übergabe-Einschreiben mit Rückschein  eigenhändig

**Zustellbestätigung**

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**Empfangsbestätigung**

|       |                        |
|-------|------------------------|
| Datum | Unterschrift Empfänger |
| ↓     |                        |

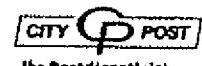
**Unzustellbar**

- nicht angetroffen
  - kein Briefkasten vorhanden
  - Annahme verweigert
  - Briefkasten überfüllt
  - Empfänger unbekannt
  - Anschrift unvollständig/falsch
  - verstorben/Firma erloschen
  - Sonstige: **Lagerfeist-Überschriften**
  - Zurück an Absender
- Strasse, Nr., PLZ, Ort
- Empfänger benachrichtigt
- Datum: **07.01.09** Unterschrift Zusteller: **Klörner**

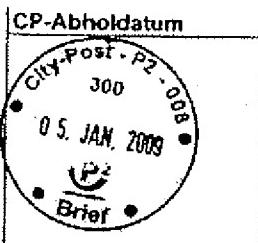
Abbildung und Zustellung erfolgt gemäß Urteil der Zuliefererorganisation

- Einwurf-Einschreiben
- Übergabe-Einschreiben
- Übergabe-Einschreiben mit Rückschein  eigenhändig

**Einschreiben**



Ihr Postdienstleister



**Absender**

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**Nummer des Einschreibens**

**C 480313**

**CP-Übernahmebestätigung**

|                        |
|------------------------|
| Datum                  |
| Unterschrift City-Post |

**Empfänger**

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Abbildung und Zustellung erfolgt gemäß Urteil der Zuliefererorganisation

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**5**

# **Exhibit 5**

(P)

Petokopie

novaled 

Novaled AG • Tatzberg 49 • 01307 Dresden

## Affidavit

I, Manuela Krumbiegel, born on April 11, 1974, resident in 01189 Dresden, Schulstrasse 14, hereby declare on oath:

1. I have been working in the position of an IP Officer for the Intellectual Property (IP) Department of Novaled AG since March 2005.

2. My responsibility is the handling of inventions originating from staff members of Novaled AG, in particular according to the prescriptions of the law relating to inventions of employees, as well as inventions Novaled AG has acquired from external parties. In this regard I was also entrusted with the handling of the invention "Use of a metal complex as n-dopand for an organic semiconducting matrix material, organic semiconducting material and electronic component and also a dopant and ligand and process for producing same" underlying the German Patent No. DE10 2004 010954.0 and the International Patent Application PCT/DE2005/00372 of which the U.S. Patent Application No. 10/585,215 was derived.

3. December 12<sup>th</sup>, 2008 I sent the *Combined Declaration and Power of Attorney* with letter to Dr. Olaf Kühl's private address asking him to sign it. To have a proof a reception I did sent it by registered mail, because Dr. Olaf Kühl had already refused to sign documents before. The letter came back un-delivered, without any notice of the post office of an incorrect address. The postman did not reach Dr. Olaf Kühl personally, but left a notice in his mailbox notifying him to pick up the letter in person. Dr. Olaf Kühl did not go to get the letter.

4. With letter dated April 1<sup>st</sup>, 2011 I have sent the *Combined Declaration and Power of Attorney* and a complete copy of said US patent application to University of Greifswald, the work address of Dr. Olaf Kühl asking him once more to sign it. The letter was sent by a courier and received by Mr(s). Groth at University of Greifswald. There was no answer until now. The information of his employment at the university I found in the internet: <http://www.uni-greifswald.de/index.php?id=14541>, [www.uni-greifswald.de/chemie/~anorgscientists.htm](http://www.uni-greifswald.de/chemie/~anorgscientists.htm)

  
Committed to excellence

Novaled AG

Phone +49(0)351 796 58-0

Fax +49(0)351 796 58-29

Board of Directors:

Gildas Sorin, Harry Böhme, Gerd Günther

Supervisory Board Chairman: Thilo von Swichow

Ostsächsische Sparkasse Dresden

Bank Account No.: 312 023 0919

B1 7- 850 503 nn.

Dresdner Bank Dresden

Bank Account No.: 4 624 269 00

B1 7- 850 000 nn.

5. On date 21<sup>th</sup> of April 2011 I called the University of Greifswald and talked to Christina Voss who is secretary of the Mathematics-Science Faculty, asking if Dr. Olaf Kühl is still employed at the University and if he did receive the letter. The secretary told me that Olaf Kühl was only employed until 31<sup>st</sup> of March 2011 but is still coming occasionally to work there and should have received the letter.

6. Because of the uncertainty that Dr. Olaf Kühl has received the letter of April 1<sup>st</sup> 2011, I called him at home and talked to his wife 24<sup>th</sup> April 2011. She told me, that Olaf Kühl cannot talk to me at the moment but I should send the documents to his private address, which I confirmed with her.

7. So I did send on the same day the *Combined Declaration and Power of Attorney* and the complete copy of the patent application text to his private address via courier service. But on 26<sup>th</sup> of April I received the message from the delivery service that Olaf Kühl has refused to take the documents and therefore the letter was returned to Novaled AG.

8. Finally, to assure that there was no misunderstanding, on May 2<sup>nd</sup> 2011 I did send an email with all the documents to two of his email addresses which I found in the internet. Olaf Kühl did not react at all.

Dresden, 08.06.2011



A handwritten signature in black ink, appearing to read "Christiane Fritze". It is written over a horizontal line.

Signature

## **Deed No. 1365 P 2011**

Sworn to and subscribed before me at Dresden this day by

Mrs. Manuela Krumbiegel, born on April 11, 1974, resident at 01189 Dresden, Schulstraße 14, who identified herself by valid German identity card.

Dresden, 2011-06-08  
(yyyy-mm-dd)

Notary

Dr. Joachim Püls  
Bärensteiner Straße 7  
01277 Dresden  
GERMANY

J.P.  
(Notary)



E  
X  
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# Exhibit 6

- Kopie - 8)



Novaled AG • Tatzberg 49 • 01307 Dresden

Universität Greifswald

Institut für Biochemie

z. Hd. Herrn Dr. Olaf Kühl

Felix-Hausdorff-Straße 4

17487 Greifswald

Dresden, 01.04.2011

**Patentanmeldung US10/585215**

Sehr geehrter Herr Dr. Kühl,

Wir haben Ihnen bereits im Dezember 2008 an Ihre damalige Adresse Dokumente zur Unterschrift zugesandt. Leider haben Sie unsere Post nicht in Empfang genommen. Ich versuche es heute noch einmal und würde mich sehr freuen, wenn Sie die beiliegende „Declaration for Patent Application US10/585215“ und das zugehörige „Assignment“ unterschreiben und an uns zurücksenden würden. Es handelt sich dabei um die übliche Erklärung an das US-Patentamt, dass Sie Miterfinder an der Patentanmeldung US10/585215 – „Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same“ sind. Ich lege Ihnen auch den Anmeldetext bei.

Bitte ändern Sie auf der Declaration die Adresse in Ihre nun gültige und zeichnen Sie die Änderung zusätzlich gegen. Vielen Dank im Voraus.

Bei Fragen erreichen Sie mich unter Tel. 0351-796 5852.

Mit freundlichen Grüßen

A handwritten signature in black ink, appearing to read "J. K." followed by a more complex, cursive name.

Manuela Krumbiegel  
IP Officer

Novaled AG • Tatzberg 49 • 01307 Dresden

Greifswald University

Institute of Biochemistry

Attn. Dr. Olaf Kühl

Felix-Hausdorff-Strasse 4

17487 Greifswald

Dresden, 1st April, 2011

**Patent application US10/585215**

Dear Dr. Kühl,

Back in December 2008, we sent you some documents for signing, mailed to your address at the time. Unfortunately, you did not accept delivery of our mail. I am making another attempt today and would be very grateful if you would sign the enclosed "Declaration for Patent Application US10/585215" and the corresponding "Assignment" and return them to us. It is the standard declaration for the US Patent and Trade Mark Office that you are a co-inventor of the patent application US10/585215 - "Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same". I also enclose the text of the application.

Please amend the address on the declaration to the one which is now valid and countersign the alteration. Many thanks in advance.

If you have any questions, you can reach me at Tel. 0351-7965852.

Yours faithfully,

Manuela Krumbiegel  
IP Officer

## **ASSIGNMENT**

The undersigned inventor, **Olaf Kuehl**, residing at Mittelstrasse 10, 04416 Markkleeberg, Germany, and for good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, does hereby sell, transfer, and assign to the Assignee, **Novaled AG**, a corporation organized and existing under the laws of Germany, and having a place of business at Tatzberg 49, 01307 Dresden, Germany, his right, title, and interest for the territory of the United States of America, in and to the invention entitled "**USE OF A METAL COMPLEX AS AN N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTING MATERIAL AND ELECTRONIC COMPONENT, AND ALSO A DOPANT AND LIGAND AND PROCESS FOR PRODUCING SAME**" as described and claimed in the application for Letters Patent filed in the United States Patent and Trademark Office on **30 June 2006**, under Application Serial No. **10/585,215**, his entire right, title, and interest in and to said application, and any non-provisional patent application based thereon, and in and to any divisions, continuations, reexaminations, and reissues thereof; and I hereby request the Commissioner of Patents and Trademarks of the United States of America to issue said Letters Patent to the Assignee, for its interest, for the sole use of the Assignee and its successors, assigns and legal representatives, as fully and entirely as the same would have been held by me had this assignment not been made;

AND, for the same consideration, I agree to sign all lawful papers, execute all division, continuing, reissue and other applications, make all assignments and rightful oaths, and generally do everything possible to aid the Assignee, its successors, assigns, and nominees, to obtain and enforce proper protection for all said inventions and improvements in the United States of America.

Date Signed: \_\_\_\_\_

**Olaf Kuehl**

**DECLARATION FOR UTILITY OR  
DESIGN  
PATENT APPLICATION  
(37 CFR 1.63)**

Declaration Submitted With Initial Filing

OR

Declaration Submitted After Initial Filing (surcharge (37 CFR 1.16(f)) required)

|                          |               |
|--------------------------|---------------|
| Attorney Docket Number   | 17346-0088    |
| First Named Inventor     | Ansgar Werner |
| <i>COMPLETE IF KNOWN</i> |               |
| Application Number       | 10/585,215    |
| Filing Date              | 30 June 2006  |
| Art Unit                 | 2815          |
| Examiner Name            | Anthony Ho    |

I hereby declare that: (1) Each inventor's residence, mailing address, and citizenship are as stated below next to their name; and (2) I believe the inventor(s) named below to be the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention titled:

**USE OF A METAL COMPLEX AS AN N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTING MATERIAL AND ELECTRONIC COMPONENT, AND ALSO A DOPANT AND LIGAND AND PROCESS FOR PRODUCING SAME**

*(Title of the Invention)*

the application of which

is attached hereto

OR

was filed on (MM/DD/YYYY) 06/30/2006 as United States Application Number or PCT International Application Number 10/585,215 and was amended on (MM/DD/YYYY) \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

**Authorization To Permit Access To Application by Participating Offices**

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the above-identified patent application is filed access to the above-identified patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the above-identified patent application is filed to have access to the above-identified patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the above-identified patent application with respect to: 1) the above-identified patent application-as-filed; 2) any foreign application to which the above-identified patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the above-identified patent application; and 3) any U.S. application-as-filed from which benefit is sought in the above-identified patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing the Authorization to Permit Access to Application by Participating Offices.

[Page 1 of 3]

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

**DECLARATION — Utility or Design Patent Application****Claim of Foreign Priority Benefits**

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed     | Certified Copy Attached? YES | Certified Copy Attached? NO |
|-------------------------------------|---------|----------------------------------|--------------------------|------------------------------|-----------------------------|
| PCTDE2005000372                     | WO      | 03/05/2005                       | <input type="checkbox"/> | <input type="checkbox"/>     | <input type="checkbox"/>    |
| 102004010954.0                      | DE      | 03/04/2004                       | <input type="checkbox"/> | <input type="checkbox"/>     | <input type="checkbox"/>    |
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|                                     |         |                                  | <input type="checkbox"/> | <input type="checkbox"/>     | <input type="checkbox"/>    |

Additional foreign application number(s) are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

**DECLARATION — Utility or Design Patent Application**

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |       |                                                                                  |                   |       |                                                       |
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| Direct all correspondence to:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |       | <input checked="" type="checkbox"/> The address associated with Customer Number: | 29052             | OR    | <input type="checkbox"/> Correspondence address below |
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| Country                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |       | Telephone                                                                        |                   | Email |                                                       |
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| I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |       |                                                                                  |                   |       |                                                       |
| NAME OF SOLE OR FIRST INVENTOR:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |       | <input type="checkbox"/> A petition has been filed for this unsigned inventor    |                   |       |                                                       |
| Given Name (first and middle [if any])                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |       | Family Name or Surname                                                           |                   |       |                                                       |
| Ansgar                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |       | Werner                                                                           |                   |       |                                                       |
| Inventor's Signature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |       |                                                                                  | Date              |       |                                                       |
| Residence: City<br>Dresden                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | State | Country<br>DE                                                                    | Citizenship<br>DE |       |                                                       |
| Mailing Address<br>Altenberger Strasse 20                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |       |                                                                                  |                   |       |                                                       |
| City<br>Dresden                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | State | Zip<br>01277                                                                     | Country<br>DE     |       |                                                       |
| <input checked="" type="checkbox"/> Additional inventors or a legal representative are being named on the <u>1</u> supplemental sheet(s) PTO/SB/02A or 02LR attached hereto                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |       |                                                                                  |                   |       |                                                       |

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| <b>DECLARATION</b>                                |       | <b>ADDITIONAL INVENTOR(S)</b><br>Supplemental Sheet                           |                   |
|---------------------------------------------------|-------|-------------------------------------------------------------------------------|-------------------|
| Page <u>2</u> of <u>2</u>                         |       |                                                                               |                   |
| <b>Name of Additional Joint Inventor, if any:</b> |       | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                   |
| Given Name (first and middle (if any))            |       | Family Name or Surname                                                        |                   |
| Olaf                                              |       | Kuehl                                                                         |                   |
| Inventor's Signature                              |       | Date                                                                          |                   |
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| <b>Name of Additional Joint Inventor, if any:</b> |       | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                   |
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| Simon                                             |       | Gessler                                                                       |                   |
| Inventor's Signature                              |       | Date                                                                          |                   |
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| Horst                                             |       | Hartmann                                                                      |                   |
| Inventor's Signature                              |       | Date                                                                          |                   |
| Dresden<br>Residence: City                        | State | DE<br>Country                                                                 | DE<br>Citizenship |
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| Dresden<br>City                                   | State | 01326<br>Zip                                                                  | DE<br>Country     |

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
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2006-06-30 JUN 2006  
PCN/P030

5       **Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same**

The invention relates to the use of a metal complex as a dopant for doping an organic semiconducting matrix material in order to alter the latter's electrical characteristics, the compound constituting an n-dopant with regard to the matrix material; it also relates to an organic semiconducting material containing an organic matrix material and a metal complex as an n-dopant, 15 and also to an electronic device with an organic semiconducting material which is doped with a metal complex as an n-dopant. The invention further relates to n-dopants and ligands and processes for producing them.

20      It is known to modify organic semiconductors with regard to their electrical characteristics, especially their electrical conductivity, by doping them, which is also the case with inorganic semiconductors such as silicon semiconductors. In the

process, charge carriers are generated in the matrix material in order to increase its conductivity, which is initially quite low, and, depending on the nature of the dopant used, to produce a change in the Fermi level of the semiconductor. In 5 this context, doping leads to an increase in the conductivity of charge transport layers, thus reducing ohmic losses, and to an improved passage of the charge carriers between the contacts and the organic layer. In organic matrix materials, inorganic dopants are generally disadvantageous because of their high 10 diffusion coefficients, since they impair the functioning and stability of the electronic devices. In addition, it is known to release dopants by means of chemical reactions in the semiconducting matrix material, in order to provide dopants. However, the oxidation potential of the dopants released in 15 this way is often not sufficient for various applications, such as for organic light-emitting diodes (OLED) in particular. Furthermore, when the dopants are released, other compounds and/or atoms are produced, such as atomic hydrogen for example, as a result of which the characteristics of the doping layer or 20 the corresponding electronic device are impaired.

What is more, organic compounds used as dopants often do not have a sufficiently low oxidation potential for the application in question.

25 The invention is therefore based on the problem of providing metal complexes as n-dopants for doping an organic semi-conducting matrix material, especially for manufacturing electronic devices, which in particular also have sufficiently 30 low oxidation potentials to produce electron transport materials for organic light-emitting diodes (OLED), without having any disturbing influences on the matrix material, and which cause an effective increase in the number of charge carriers in the matrix material and are preferably 35 comparatively easy to handle. In addition, it is an object of the invention to provide suitable ligands and processes for

producing the dopants.

These objects are achieved by the features of the independent claims, in particular by the use of neutral electron-rich metal complexes. In addition, the problem is solved by the provision of an organic semiconducting material with a compound of a neutral electron-rich metal complex of this kind as an n-dopant. Preferred embodiments can be learned from the dependent claims.

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As a consequence of the fact that an electron-rich metal complex is used in a neutral form as an n-dopant vis-à-vis the organic semiconducting matrix material, there is a considerably stronger donor available than in organic donor compounds known hitherto. Furthermore, compared to other n-dopants in the form of organic compounds, the provision of a neutral electron-rich metal complex makes it possible to vary the donor characteristics of the compound by selecting a suitable central atom, and thus to vary its oxidation potential. The n-dopants of the invention thus preferably have a very low oxidation potential. The complex preferably has at least one organic ligand, without being restricted to that. In particular, the use of the n-dopants of the invention can substantially increase the conductivity of charge transport layers, and/or the passage of the charge carriers between the contacts and the organic layer can be improved considerably in applications as electronic devices.

The metal complexes used in accordance with the invention are preferably isolated molecules, which are thus preferably present in the semiconducting layer concerned as isolated molecules that are not immobilised by chemical bonds among each other and/or by being bound to a matrix and/or to another component. The valence electrons of the metal central atoms, with the exception of the valence electrons of the complex which are associated directly with the metal atom, are thus

preferably provided substantially or completely by the ligands of the complex and the metal atoms of the complex, these being arranged within the coordination sphere formed by the ligands, which is preferably at least substantially closed. Preferably, 5 all the metal atoms of the complex or all the metal atoms of an outer sphere of the metal complex are co-ordinated to non-metallic ligands, preferably organic ligands. It goes without saying that individual metal complexes may in each case be bound to one another or to other components, such as the matrix 10 material, in order optionally to immobilise the metal complexes. For this purpose, the ligands may, for example, possess suitable functional groups that can be linked together, such as unsaturated groups, which may react with one another in a linear or branched manner to form an oligomer or polymer.

15

The complexed central atom may have a formal number of valence electrons VE of 16 or more, such as 18 or 19 or 20 or 21 or more valence electrons. The central atom may in this case in particular be a metal atom from the first transition metal 20 period, a metal atom from the second transition metal period or a metal atom from the third transition metal period. Independently thereof or in combination with it, the complexes of the invention may be at least binuclear complexes with at least one metal-metal bond between the central atoms, as a 25 result of which particularly electron-rich metal complexes with a high electron density at the central atom of the metal complex can be provided in each case.

It is particularly preferred to have a neutral or charged 30 transition metal atom as the central atom of the electron-rich metal complex. The central atom may, for example, be a metal atom from the group of the first transition metal period (scandium to zinc), or a metal from the second transition metal period (yttrium to cadmium), e.g. rhodium, palladium, silver 35 and cadmium, or a metal from the third transition metal period, including lanthanides and actinides. The central atom may in

- particular be a metal from the 7th to 10th groups. The transition metal of the at least one central atom may also be one of the following elements in each case: V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nd, Ta, Mo, W, Rh, Ir, Pd, Pt. The transition metal
- 5 atom is particularly preferably selected from the group Mn, Fe, Co, Ni, Cu, Zn, e.g. selected from the group Fe, Co, Ni. In addition, the transition metal atom may be selected from the group Cr, Mo, W. The transition metal atom may also be selected from the group V, Nb, Ta or the group Ir, Pt, Au, Hg. For
- 10 various intended uses, however, metal complexes with a smaller formal number of valence electrons at the metal central atom of the complex, or with a lower electron density at the metal central atom may also be used.
- 15 In the neutral metal complex used in accordance with the invention, the transition metal atom may be present as a neutral atom or as a charged transition metal atom, preferably with a formal charge of 0 to 3, e.g. a formal charge of 0, 1 or 2, it being in particular possible for the central atom to be an atom
- 20 from the first transition metal period. The charge of the central atom, which may be an atom from the first, second or third transition metal periods, may also be different from 0.
- At least one, two or more, or all of the ligand atoms (donor atom) binding to the central atom may be different from an aromatic nitrogen atom which is part of an aromatic 6-membered ring, in which the nitrogen atom has a double bond with a neighbouring atom, especially a carbon atom. In complex
- 25 chemistry, pyridine, pyrimidine, pyridazine or pyrazine are often used as such ligands. At least one, two or more, or all of the ligand atoms binding to the central atom may optionally also be different from an aromatic nitrogen atom of a 5-membered ring, such as a pyrrole or imidazole ring, for example. In these cases, however, the aromatic ring of the
- 30 substituent may not have a co-ordinating nitrogen atom or a substituent with an N atom. In particular, at least one ligand
- 35

atom binding to at least one central atom may be present which is different from the nitrogen atom of a pyridine, 2,2';6',2''-terpyridine or 2,2'-bipyridine, in particular different from 4,4',5,5'-tetramethyl 2,2'-bipyridine. What has been said above 5 may in each case apply to substituted or unsubstituted ligands. In particular, what has been said above may apply to Cr or Ru complexes. It goes without saying, however, that ligands of this kind are not generally excluded from the invention; optionally, one, two or more, or all of the donor atoms may 10 have the above-mentioned characteristic.

In particular, at least one ligand may also be at least bidentate or tridentate, and at least one, two or more of the donor atoms of the ligands binding to a central atom can be 15 different from nitrogen.

At least one, two or more donor atoms of the at least one ligand, or 1, 2, 3 or 4 or more, or all of the donor atoms of the complex may, for example, be an  $sp^3$ -configured nitrogen 20 atom, such as the nitrogen atom of a substituted or un-substituted alkylamine moiety which is not also encompassed by what has been said above. One, two or more, such as 3, 4 or all, of the ligand atoms binding to at least one central atom of the neutral metal complex may optionally be different from 25 an aromatic nitrogen atom or different from nitrogen in general. Independently of this or at the same time, one, two, three, four or more, or all of the donor atoms of at least one or all of the central atoms of the complex may be different from oxygen, without this being compulsory.

30 Preferably, at least one ligand atom binding to the central atom is selected from the group consisting of B, Al, Ga, In, C, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te and optionally also O, where 2, 3, 4 or more, or all of the ligand atoms binding to 35 the central atom may be selected from that group. Preferably, at least 1, 2, 3 or 4 or more, or all of the donor atoms are

selected from the group consisting of B, C, Si, Ge, Sn, S, P, Se, As, Sb, Te (optionally including N), in particular selected from the group B, C, S, P, Se (optionally including N). It goes without saying that, in addition, at least one of the ligand atoms may in each case also be selected from the group Si, Ge, Sn, As, Sb, Te.

At least 1, 2, 3 or 4 or more, in particular also all of the ligand atoms binding to the central atom may also have a lower electronegativity than nitrogen (electronegativity according to Allred-Rochow for N: 3.07).

It goes without saying that the above statements regarding the ligand atoms binding to the central atom (donor atoms) apply to mononuclear metal complexes, but also to polynuclear metal complexes in which the ligand atom binding to the central atom may bind to only one central atom, but also to two or three central atoms, for example, in the case of a polynuclear complex. In this case, the ligand concerned may be a monodentate ligand or also a bidentate, tridentate or polydentate ligand, where different ligand atoms may bind to different metal atoms of the metal complex of the invention and may, in the process, form bridging ligands, for example. It also goes without saying that, in the case of polynuclear metal complexes with preferably two, but also with three or more central atoms, which in each case are preferably transition metal atoms, which may be neutral or charged, metal-metal bonds can exist between two or more central atoms. As far as the valence electrons are concerned, these metal-metal bonds may formally correspond to a single bond but also optionally to a metal-metal multiple bond, though a metal-metal bond may also be present whenever the electron density between the metal atoms is lower than that for a metal-metal single bond. It goes without saying that the other metal atoms of a polynuclear metal complex are not to be understood as ligand atoms for the purposes of the invention.

At least 1, but optionally also 2, 3 or 4 or more, or all of the donor atoms of the metal complex may be components of a heterocyclic unsaturated ring, where the heteroatom is preferably the atom binding to the central atom of the metal complex. The heteroatom can in particular be an N, S, P or Se atom, but optionally also an O atom, though without being restricted to that. The heterocyclic unsaturated ring may optionally contain further heteroatoms, which may also be different from the first heteroatom. The metal complex can have 1, 2, 3, 4 or more, or all of the ligand atoms as components of such a heterocyclic unsaturated ring. The heterocyclic unsaturated ring may have 5, 6 or 7 ring atoms, though without being restricted to that.

15

Preferably, 1, 2, 3, 4 or more, or all of the donor atoms of the complex are components of an aromatic ring or a conjugated - e.g. mesomeric - system of the ligand, wherein the donor atom can bind, for example, to one or two multiply bonded atoms.

20

In the following, some advantageous classes of compounds will be described in more detail:

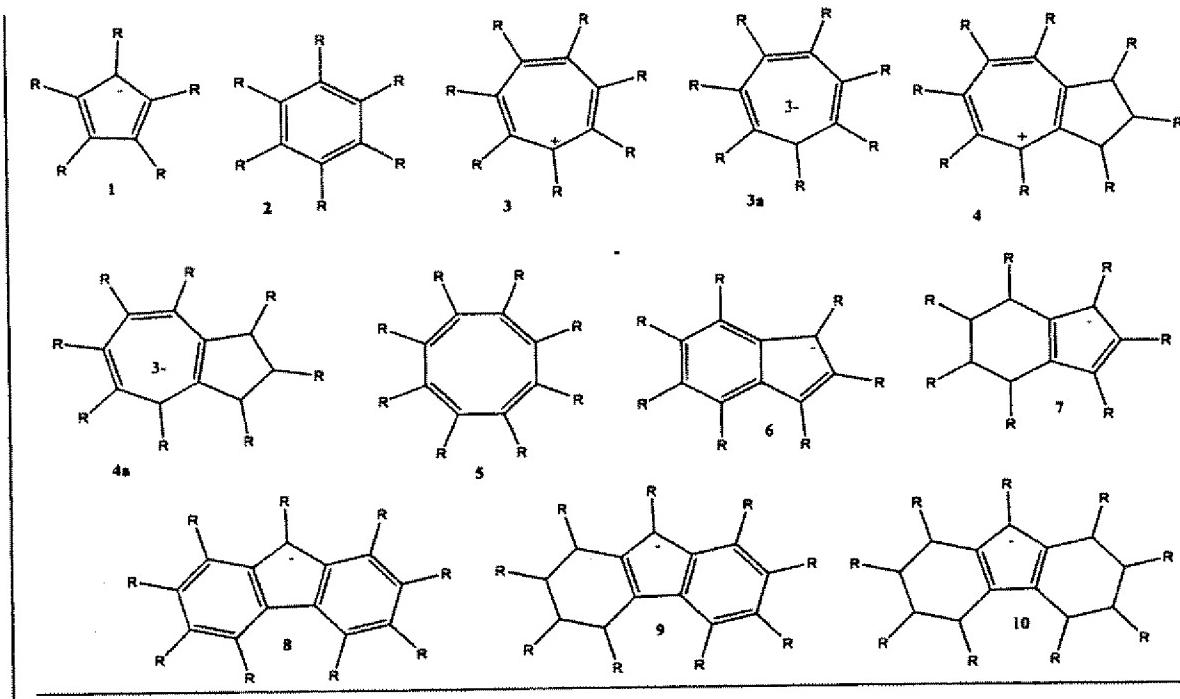
### $\Pi$ complexes

According to one advantageous embodiment, at least one ligand of the neutral metal complex forms a  $\Pi$  complex with the central atom. The ligand of the  $\Pi$  complex can co-ordinate with a multiple bond, i.e. a double bond or triple bond, to the central atom, where the multiple bond may, for example, be a C-C, C-O, C-N, S-O, N-O, though without being restricted to that. The ligand forming the  $\Pi$  complex may have a mesomeric or aromatic system which forms the  $\Pi$  complex with the central metal atom. The  $\Pi$  complex may, for example, contain a 2-electron donor such as a double or triple bond, a 3-electron donor such as an allyl group or an  $\eta^3$ -1-3-cyclohexenyl group, a 4-electron donor such as a butadiene or cyclobutadiene group, a

5-electron donor such as an  $\eta^5$ -1,5-cyclohexadienyl group or in particular a 6-electron donor group such as a benzene nucleus, a cyclopentadienyl anion, a cycloheptatrienyl cation, cycloheptatrienyl tri-anion, cyclo-octadienyl di-anion or the like. It goes without saying that the complex may also have two or more ligands that form a  $\pi$  complex with the central atom. In particular, the complex may comprise two ligands forming a  $\pi$  complex with the central atom, which can co-ordinate the central atom, in particular in a linear manner. It goes without saying that the  $\pi$  complex may also comprise further ligands, which do not co-ordinate with the central atom via a  $\pi$  electron system. Ligands of this kind may, for example, be carbonyl, phosphines or the like, without being restricted to these. It further goes without saying that the  $\pi$  complex may also have two or optionally more ligands co-ordinating with the central atom via a  $\pi$  bond system, these ligands being different from one another, in particular with regard to the number of electrons in the  $\pi$  electron system and/or with regard to the number of co-ordinating atoms, in particular the number of ring atoms in the case of aromatic  $\pi$  complexes. The central atom may, for example, be co-ordinated by a  $\pi$  benzene ligand and/or a  $\pi$  cyclopentadienyl ligand or by two  $\pi$  cyclopentadienyl ligands or two  $\pi$  benzene ligands, such as dibenzene iron, which are differently substituted, or by a cyclopentadienyl or benzo ligand on the one hand, and a ligand complexing via a double or triple bond on the other, where the double or triple bond may optionally also have a heteroatom. As  $\pi$  complexes, the bis-cyclopentadienyl complexes may be  $\eta^5$  complexes, though without being restricted to that.

In general, one, more than one or all of the ligands of the complex may be selected from group 1-10 (with compound 5 in particular as a singly or doubly charged anion or cation). In the parent compounds 1-10, one or more than one or possibly even all of the C, CR, CR<sub>2</sub>, C<sup>-</sup>, CR<sup>-</sup>, CR<sub>2</sub><sup>-</sup> groups may be iso-electronically or non-isoelectronically substituted by appro-

priately identical or different heteroatoms. In particular, one or more than one of the groups CR or C<sup>-</sup> may be replaced by P. At the same time or alternatively, one or more than one of the groups CR<sub>2</sub> or CR<sup>-</sup> may be replaced by S. The following elements 5 may be used as heteroatoms: B, Al, Ga, In, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, O, S, Se, Te, optionally also without O. In particular, the heteroatoms may be selected from the group B, Al, Ga. Furthermore, the heteroatoms may be selected in particular from the group N, P, As, Bi, preferably selected 10 from the group N, P, As. In addition, the heteroatoms may be selected from the group Si, Ge, Sn, Pb, in particular from the group Si, Ge. Also, the heteroatoms may be selected from the group O, S, Se, Te, in particular from the group O, S, Se. In particular, the heteroatoms from the groups mentioned may also 15 in each case be atoms of the third main group period (atomic numbers in particular between 13 and 16) or the fourth main group period (atomic numbers in particular between 31 and 34).



The groups R in the parent compounds 1-10 may be the same or different, open-chain or components of a ring or ring system, and are preferably selected from: alkyl, including cycloalkyl, aryl, or the above heteroatoms. The alkyl or aryl groups may be 5 completely or partially substituted with one or more heteroatoms from the above list, which may be the same or different. It goes without saying that the above groups R, but also quite generally groups in accordance with the invention, may be ones with a +I effect and/or +M effect on an unsaturated or aromatic 10 ring (or P instead of N). Generally speaking, the R groups in compounds according to the invention may also have unsaturated groups, e.g. with C=C, C=N bonds or the like.

The central atom of the complexes may in each case be selected 15 from the group Mn, Fe, Co, Ni, Cu, Zn or the group Cr, Mo, W, particularly preferably those selected from the group Fe, Co, Ni, such as complexes with Fe or Co. The central atom may also be a different metal atom from groups 6 or 7 to 10.

20 In particular, 1, 2 or all of the ligands may in each case be cyclopentadienyl or benzene or may be selected from the group of compounds 3, 4 and 5 or from the group of compounds 6, 8 and 9, in particular also compound 8, or selected from the group of compounds 7, 10, where the ligands may in each case be substituted or unsubstituted.

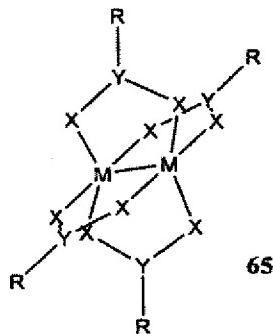
#### Paddlewheel complexes and polynuclear complexes in general

According to one advantageous embodiment, the metal complex of the invention is a polynuclear metal complex. In particular, 30 the metal complex may be a polynuclear metal complex with at least one, two, three or four or optionally even more ligands which bind to at least two metal central atoms. The metal complex may in this case also have one, two or more metal-metal bonds, which may in each case be metal-metal single bonds or 35 metal-metal multiple bonds. The polynuclear complex may have two, three or even four or more metal central atoms. The com-

plex preferably does not contain more than 20 or not more than 10 metal atoms or not more than 6 or 4, in particular not more than 3 metal atoms. The metal complexes are in each case preferably isolated molecules. Polynuclear complexes may in particular be carbonyl or cyclopentadienyl complexes.

The metal atoms of polynuclear metal complexes are preferably mainly or entirely transition metal atoms, in particular from the 6th or 7th to 10th groups, selected, for example, from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W.

A metal complex of this kind may, for example, be a so-called paddlewheel complex 65, wherein two metal central atoms, in particular transition metal central atoms are bridged by 1, 2, 3, 4 or more bidentate ligands which in each case bind one ligand atom to both metal central atoms. The metal atoms in this case are usually co-ordinated 4-fold or optionally even 5-fold or higher:



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One or both metal central atoms M may optionally also be complexed, in each case independently of one another, with at least one further ligand, such as carbonyl, phosphine or others, which may in particular be disposed axially (terminally) to the M-M bond.

In particular, the polynuclear metal complexes may have at least one atom from the group Mn, Fe, Co, Ni, Cu, Zn, in par-

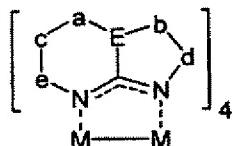
ticular an atom from the group Fe, Co, Ni or at least one atom selected from the group Cr, Mo, W, in particular also Mo, W, where preferably all the central atoms of the neutral metal complex are identical. In general, M can be any metal atom at 5 all, in particular a transition metal atom, such as a transition metal atom from the first, second or third transition metal periods or an atom from the 6th or 7th to 10th transition metal groups. In this context, both metal atoms M can in each case be the same or different from one another.

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Instead of the bidentate ligands RYX<sub>2</sub> bridging the two metal central atoms together, it is also possible for one or more of the bridge ligands to be replaced by monodentate ligands, such as by carbonyl, RCN, substituted or unsubstituted phosphines or 15 others, where the substituent R can be any organic residue including hydrogen, in particular also a hydrocarbon residue or a substituted or unsubstituted alkyl residue, in particular a C<sub>1</sub> to C<sub>10</sub> alkyl residue, in particular C<sub>1</sub> to C<sub>4</sub> or to C<sub>6</sub>.

20 At least one, more or all of the ligand atom(s) X binding to the metal atom may be selected from the group F, Cl, Br, I, O, S, Se, N, P, such as halogen, preferably selected from the group O, S, Se, N, P, particularly preferably selected from the group S, Se, N, P, where at least one, two, three or four or 25 all of the ligand atoms can be different from N. X may, however, also be a different suitable atom. The various atoms X binding to the metal atom can be the same or different within a ligand or within the complex. This means that different ligands L, L' may also be used as bidentate ligands bridging the two metal atoms. The atom Y is preferably an element from the main group, in particular a bi-, tri- or tetracovalent element from the main group. The atom Y is preferably selected from the group B, C, N, O, Si, P, S, As, Se, Sb, Te, especially preferably selected from the group O, S, Se, N, P, C, in 30 particular selected from the group S, Se, N, P (optionally also O), without being restricted to these.

- Preferably, at least one ligand, two, more or all of the ligands are selected from the group of halides, carboxylates, formamidinates, pyrimido-pyrimidines including their anions, in particular substituted or unsubstituted pyrimido[1,2-a]pyrimidine or their anions, in particular hpp (hpp: anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine), and guanidinates, optionally also diketonates. In this context, the ligands can in each case be the same or different from one another. In particular, at least one ligand is a carboxylate, a formamidinate, a pyrimido-pyrimidine, in particular hpp, or a guanidine. In particular, all the ligands of the complex are in each case a carboxylate, a formamidinate, a pyrimido-pyrimidine, in particular hpp, or a guanidine, all the ligands of the complex preferably being the same. The ligands are particularly preferably selected from the group of carboxylates, formamidinates, pyrimido-pyrimidines and guanidinates. The Y and also X groups, especially carboxylates, formamidinates, pyrimido-pyrimidines and guanidinates, optionally also diketonates, can each be substituted or unsubstituted; they may, for example, have substituted or unsubstituted alkyl residues or hydrocarbon residues, for example in each case with C1 to C10 or higher, in particular C1 to C6 or C2 to C4, or other substituents.
- At this point, however, and also generally in the context of this invention, the term "alkyl residue" also comprises cycloalkyl residues, in particular cycloheptyl, cyclohexyl or cyclopentyl residues.
- Of the list given above, the structural types 65a, 65b, 65c and 65d are preferred, and these will be described in more detail in the following:



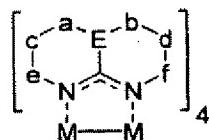
## Type 65a

where

- 5        - the structural elements a-e may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$  and e =  $-CR_9R_{10}-$ , where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> are, at the same time or independently of one another, H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR; preferably, R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, or
- 10      - optionally, a or b or e or d may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, or
- 15      - optionally, a and d or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, or
- 20      - at c, C is replaced by Si,
- wherein the bonds b-d and c-e or b-d and a-c can, at the same time or independently of one another, be unsaturated,
- 25      - wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another, be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 30      - wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- 35      - wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,

- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 5 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N, ,
- wherein the metal M is a transition metal, preferably W or Mo;

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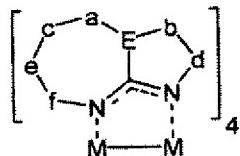
Type 65b

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where

- the structural elements a-f may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$ , e =  $-CR_9R_{10}-$  and f =  $CR_{11}R_{12}$ , where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are hydrogen,  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl,  $-NR_2$  or  $-OR$ ; preferably  $R_1$ ,  $R_3$ ,  $R_5$ ,  $R_7$ ,  $R_9$ ,  $R_{11}$  = H and  $R_2$ ,  $R_4$ ,  $R_6$ ,  $R_8$ ,  $R_{10}$ ,  $R_{12}$  =  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl,  $-NR_2$  or  $-OR$ , the structure 65b with  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  = H being excluded from this, or
- 20 - in the structural elements c and/or d, C may be replaced by Si, or
- optionally, a or b or e or f may be NR with R =  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl, or
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- optionally, a and f or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl,
- wherein the bonds a-c, b-d, c-e and d-f, but not simultaneously a-c and c-e and not simultaneously b-d and d-f may be unsaturated,
- wherein the bonds a-c, b-d, c-e and d-f can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, b-d, c-e and d-f may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;



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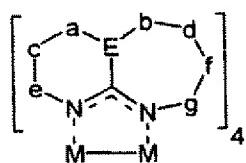
Type 65c

where

- the structural elements a-f may mean: a =  $-\text{CR}_1\text{R}_2-$ , b =  $-\text{CR}_3\text{R}_4-$ , c =  $-\text{CR}_5\text{R}_6-$ , d =  $-\text{CR}_7\text{R}_8-$ , e =  $-\text{CR}_9\text{R}_{10}-$  and f =  $\text{CR}_{11}\text{R}_{12}$ , where  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$ ,  $\text{R}_{11}$  and  $\text{R}_{12}$  can, at the same time or independently from one another, be H,  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_1\text{-C}_{20}$  cycloalkyl,  $\text{C}_1\text{-C}_{20}$  alkenyl,  $\text{C}_1\text{-C}_{20}$  alkinyl, aryl, heteroaryl,  $-\text{NR}_2$  or  $-\text{OR}$ ; preferably  $\text{R}_1$ ,  $\text{R}_3$ ,  $\text{R}_5$ ,  $\text{R}_7$ ,  $\text{R}_9$ ,  $\text{R}_{11}$  = H and  $\text{R}_2$ ,  $\text{R}_4$ ,  $\text{R}_6$ ,  $\text{R}_8$ ,  $\text{R}_{10}$ ,  $\text{R}_{12}$  =  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_1\text{-C}_{20}$  cycloalkyl,  $\text{C}_1\text{-C}_{20}$  alkenyl,  $\text{C}_1\text{-C}_{20}$  alkinyl, aryl, heteroaryl,  $-\text{NR}_2$  or  $-\text{OR}$ , or
- 5 - at c or e, C may be replaced by Si, or
- optionally, a or b or d or f may be NR with R =  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_1\text{-C}_{20}$  cycloalkyl,  $\text{C}_1\text{-C}_{20}$  alkenyl,  $\text{C}_1\text{-C}_{20}$  alkinyl, aryl, heteroaryl, or
- optionally, a and d or b and f may be NR with R =  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_1\text{-C}_{20}$  cycloalkyl,  $\text{C}_1\text{-C}_{20}$  alkenyl,  $\text{C}_1\text{-C}_{20}$  alkinyl, aryl, heteroaryl,
- 15 - wherein the bonds a-c, c-e, e-f and b-d, but not simultaneously a-c, c-e and e-f and not simultaneously a-c and c-e and not simultaneously c-e and e-f may be unsaturated,
- 20 - wherein the bonds a-c, c-e, e-f and b-d can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, e-f and b-d may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- 25 - wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- 30 - wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or

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Type 65d

- wherein the structural elements a-g may mean: a = -CR<sub>1</sub>R<sub>2</sub>-, b = -CR<sub>3</sub>R<sub>4</sub>-, c = -CR<sub>5</sub>R<sub>6</sub>-, d = -CR<sub>7</sub>R<sub>8</sub>-, e = -CR<sub>9</sub>R<sub>10</sub>-, f = CR<sub>11</sub>R<sub>12</sub> and g = CR<sub>13</sub>R<sub>14</sub>, where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub> can, at the same time or independently from one another, be H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR; preferably, R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub>, R<sub>13</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub>, R<sub>14</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, or
- at c, d and f, though not d and f simultaneously, C may be replaced by Si, or
- optionally, a or b or e or g may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or
- optionally, a and g or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl,
- wherein the bonds a-c, c-e, b-d, d-f and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d,

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- d-f and f-g, and not simultaneously b-d and d-f, and not simultaneously d-f and f-g, may be unsaturated,
- wherein the bonds a-c, c-e, b-d, d-f and f-g can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
  - the bonds a-c, c-e, b-d, d-f and f-g may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
  - wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
  - wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
  - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N
- wherein the metal M is a transition metal, preferably W or Mo.

For the residues R in the structures 65a-65d, the definitions for the structure 65, as described above, can be used.

The ligands which are used to produce structures 65a-65d are also in accordance with the invention.

30 Further complex ligands

Preferably, at least one, two or more, or all of the ligands are selected from the group of borates, carboranes, triaza-cycloalkanes, triazacycloalkenes, pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles, oxazoles, pyridines, pyridazines, 35 pyrimidines, pyrazines. In particular, at least one, two or

more, or all of the ligands are selected from the group of borates, carboranes. At least one, more or all of the ligands may be selected from the group of triazacycloalkanes, triaza-cycloalkenes, optionally also other amines. At least one, two 5 or more or all of the ligands may be selected from the group of pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles and optionally oxazoles. At least one, two or more or all of the ligands may be selected from the group of pyrines, pyridazines, 10 pyrimidines, pyradzines. The ligands may in each case be the same or different and may in each case be selected from one of the groups mentioned or from more than one of the groups mentioned. In particular, whenever a ligand is selected from the group of borates and carboranes, another ligand may be an arene or arenyl n-ligand, such as a substituted or unsubstituted cyclopentadienyl, benzene or cycloheptatrienyl ion, for example. 15

The central atom of the respective complex may in each case be selected from the group Mn, Fe, Co, Ni, Cu, Zn or selected from the group Cr, Mo, W, particularly preferably selected from the 20 group Fe, Co, Ni, such as complexes with Fe or Co. The central atom may also be a metal atom from groups 6 or 7 to 10.

#### Carboranes

Preferred carboranes are those of the type  $[R_2C_2B_4]^{+}$ ,  $[R_2C_2B_9H_9]^{2-}$ , 25  $[R_2C_2B_{10}H_{10}]^{2-}$ , where R may be any substituents, in particular alkyl substituents, in particular lower alkyl substituents with C<sub>1-6</sub>. The substituents R may in each case be the same or different.

#### Borates

If the ligand is a borate anion, the borate preferably possesses the general structure 15 (Table 2), where R is any substituent, preferably H, alkyl, in particular lower alkyl with C<sub>1-C6</sub> or aryl, in particular benzyl, or a hydrocarbon residue in 35 general. It goes without saying that the substituent R may also possess heteroatoms, in particular N, O or halogen. R' is any

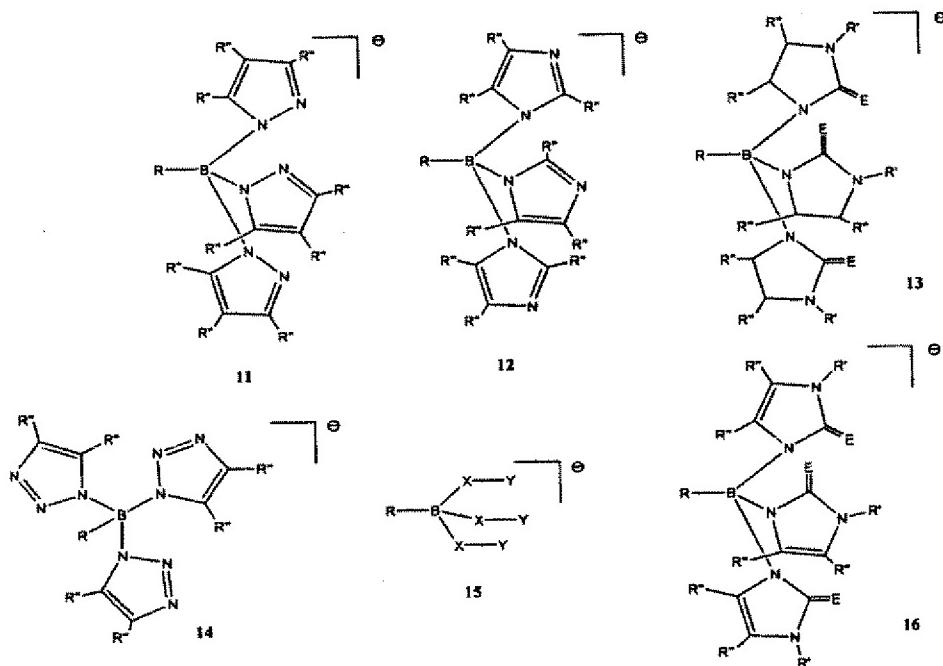
substituent, preferably alkyl, in particular lower alkyl with C<sub>1</sub> to C<sub>6</sub> or aryl, where R' may possess heteroatoms such as, in particular, N, O, halogen. R' may also be a pure hydrocarbon. For R'', the statements regarding R apply. The various substituents R, R' or R'' may in each case be the same or different. Two substituents R'' may be part of a ring system, in particular part of an identical ring system, preferably part of a ring system fused to the skeleton, or parent structure. The ring system may be saturated, unsaturated, in particular aromatic. E is an at least divalent atom and may be selected from the group O, S, Se, Te, optionally selected from the group O, S, Se or selected from the group S, Se and Te. The group E of the various ring systems may in each case be the same or different. X is a "spacer", where optionally 1, 2 or 3 of the X groups may be missing in the compound 15. X may be a branched or unbranched alkyl chain with or without heteroatom substituents, in particular an alkyl chain with 1 to 6, especially C<sub>1</sub> to C<sub>4</sub> or C<sub>1</sub> to C<sub>2</sub>, an aryl substituent, including a heterosubstituted aryl substituent, a fused aryl substituent with or without heteroatoms, an alkyl aryl substituent with or without a heteroatom or a heteroatom. The heteroatom is in each case preferably selected from the group N, P, S, Se, Ge, Sn, without being restricted thereto. The various groups X in the compound 15 may in each case be the same or different. X is preferably an alkyl chain, particularly preferably a lower alkyl chain with C<sub>1</sub> to C<sub>6</sub>. Y is a heteroatom or carbon atom capable of acting as a donor, preferably selected from the group N, P, S, Se, Ge, Sn, optionally selected from the group N, P, S, Se or selected from the group P, S, Se, Ge, Sn. In compound 15, the various donor atoms Y may in each case be the same or different. Y may be part of a ring or a ring system, in particular an unsaturated ring or ring system, including an aromatic or heteroaromatic ring system. The ring possessing the hetero or carbon atom Y capable of acting as a donor preferably comprises 5 to 7 ring atoms, such as 5 or 6. The ring containing the donor atom Y may in each case have more heteroatoms, which can

be the same or different, such as two or three. The heteroatoms may in each case be N atoms, for example, or possess at least one N atom.

- 5 In particular, the borate may possess fewer than three, two or one, or no oxygen-donor atom.

In particular, the borate may be one of the compounds 11, 12, 13, 14 or 16, wherein the metal complex may also possess different borate ligands, in particular different borate ligands from said group of compounds 11, 12, 13, 14, 16.

In this context, the Y atom, like borates in general, especially borates according to compound 15, may in each case also be a component of a pyrrole, indole, carbazole, furan, benzofuran, thiophene, benzothiophene, pyradzole, imidazole, thiazole, or oxazole ring. One or more of the Y atoms can also be components of a pyridine, quinoline, isoquinoline, acridine, pyridazine, pyrimidine, pyrazine, quinoxaline, pteridine, or purine ring, wherein the donor atom Y binding to the central atom may be a component of a 5 or 6-membered ring. In general, Y may be a component of a (hetero)aromatic ring. Said rings may in each case also be partially or fully saturated. In general, Y may be a component of a 3 to 8-membered, especially 3, a 3 to 6-membered, in particular 5 or 6-membered ring. Y may, in particular as a ring, possess the heteroatoms O, N, P, S, Se, Ge, Sn, especially the heteroatoms O, N, P, S. C may form a carbanion in this context; C, Ge and Si may form carbenes (C(II)), germynes (Ge(II)) and silylenes (Si(II)). The ring preferably has one or two multiple bonds which are in conjugation with the donor atom Y.



It goes without saying that the residues Y in the compound 15 may be the same or different.

5

Proceeding from the compound 15 or from one of the compounds 11, 12, 13, 14 or 16, the borate may optionally also be only a bidentate or even only a monodentate ligand, in which one or two of the X-Y groups are replaced in each case by one substituent R, independently of one another, including H, where two substituents R may also form a saturated or unsaturated ring. In the process, the tridentate borate ligands may co-ordinate, especially facially, to the central atom.

15 In the compound 15, the B atom may optionally also be replaced by an Al or Ga atom.

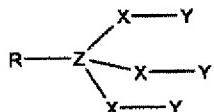
The central atom of the carborane or borate-metal complexes, in particular the compounds 11, 12, 13, 14, 16, can preferably be selected from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, especially from the group Fe, Co, Ni; the metal atom can also be selected from the group Cr, Mo, W; it may be Cr, Mo or W, for example,

or a metal from the transition metal groups 7 to 10.

Tripod ligands

According to a further advantageous embodiment, at least one,

- 5 two or all of the ligands of the neutral metal complex may be tripod ligands 18, which thus possess three ligand atoms,



18

which bind to at least one central metal atom of the complex concerned and bind to a central atom via further atoms or groups, which have the function of spacers. Compounds according to formula 15 are tripod ligands of this kind. It goes without saying, however, that the central B atom of compound 15, for example, can be replaced by a C, Si, P or As atom, though without being restricted to that. In general, the tripod ligand according to formula 18 may possess a suitable central atom Z, which may be an element from the main group, but also a transition metal atom. Independently thereof, Z can be a metal atom, in particular also a metal atom from the main group. Z is an at least trivalent atom. Z is preferably carbon, but it may in particular also be B or P. As to the rest, what has been stated above with regard to the borates applies to the groups R, X and Y. In particular, the groups -X-Y may also be formed in accordance with the compounds 11, 12, 13, 14 and/or 16.

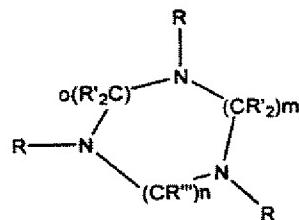
- 25 In particular in the tripod ligand, Y is generally also an atom capable of acting as a donor, which may be a heteroatom or a carbon atom. At least one, more or all of the heteroatoms of the tripod ligand are preferably selected from the group N, P, S, Se, Ge, Sn, optionally also Si, though without being restricted to that. The donor atom may in each case carry a charge, especially a negative charge; it may, for example, be a carbanionic carbon. The donor atom may also occur in a lower valency than its maximum valency; it may, for example, be a

carbene-carbon atom, a germylene-germanium atom, a silylene-silicon atom, a Sn(II) or even a Pb(II) atom. Preferably, at least one donor atom of the ligand is a carbanion-carbon atom or an atom with lower than its maximum valency, especially C, 5 Ge, Si; this applies particularly preferably to all the donor atoms of the ligand. Y may optionally also be a component of a ring or ring system. The donor atoms of the tripod ligand are preferably the same as one another, but they may also be different from one another.

10

The ligand preferably has at least one or two donor atoms as the carbanion-carbon atom binding to at least one metal central atom or, with regard to the ligand, a formally divalent atom selected from the group C (carbene), Si (silylene), Ge (germylene), 15 optionally also Sn or Pb, which are in each case components of an aromatic or non-aromatic, preferably unsaturated ring, where the multiple bond may be in conjugation with the free electrons of the donor atom. The ring possessing the donor atom preferably has at least one or two further heteroatoms, 20 preferably selected from the group N, P, As, S, Se or Te, especially N, S, Se, which may be the same or different in each case.

#### Triazacycloalkanes



17

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One, two, more or all of the ligands of the metal complex of the invention may be triazacycloalkanes, especially those of the general formula 17, where m, n, o are integers, preferably 30 integers from 0 to 6 independently of one another in each case, preferably from 0 to 4, particularly preferably 1 or 2 inde-

pendently of one another in each case. m, n and o may be the same or different from one another in each case. Substituents R can be any residues, preferably alkyl residues, especially lower alkyl residues with C1 to C6, or aryl residues, including hydrogen. The alkyl or aryl residues may be substituted or unsubstituted. The residues may be the same or different in each case. All or several of the substituents R may be free electron pairs, as a result of which the ligand formally receives one or more negative charges. The residues R' may be any substituents, preferably hydrogen, alkyl or aryl; as for the details in this context, the statements concerning the residue R apply *mutatis mutandis*. The various residues R' may be the same or different. It goes without saying that one or more of the N atoms of the triazacycloalkanes may also be replaced by an atom selected from the group P, As, Sb. Triphosphacycloalkanes are preferred here.

It also goes without saying that, in the event that m, n and/or o are integers of 2 or greater, the above-mentioned groups between the heteroatoms of the cyclic ligands may also be unsaturated, for example forming triaza(hetero)cycloalkenes, dialkenes, trialkenes or the like. The alkyl or aryl residues of the substituents R and/or R' may in each case also possess heteroatoms.

25

#### Fullerenes

In addition, complexes are preferred in which at least one, two or all of the ligands are Buckminster fullerenes, which bind to the central atom of the complex. The Buckminster fullerenes may in particular be C<sub>60</sub> and/or C<sub>70</sub> fullerenes. Derivatives of these fullerenes, especially substituted fullerenes, are thus also encompassed hereby. In this context, the fullerenes ultimately constitute substituted cyclopentadienyl ligands, since the latter complex the central metal atom via the cyclopenta-dienyl ring.

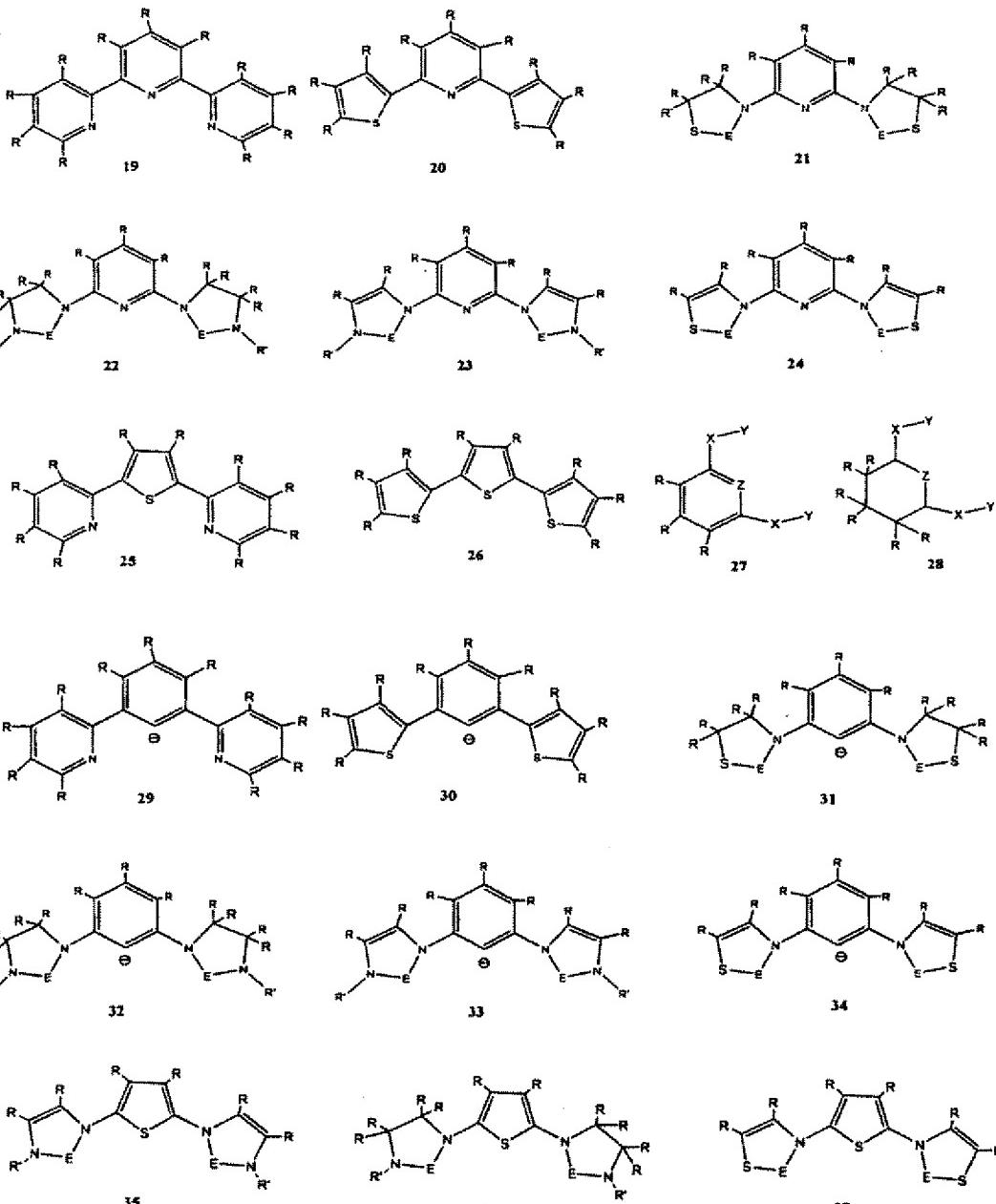
Pincer ligands

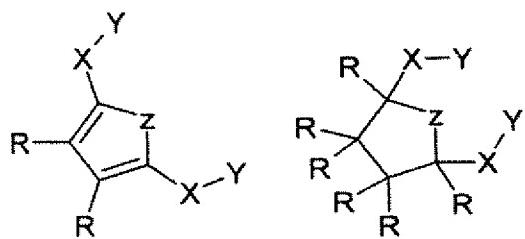
In addition, so-called pincer ligands, which act as tridentate ligands vis-à-vis the central metal atom of the complex, are particularly preferred. In particular, such pincer ligands may be bound meridionally to the central atom. The pincer ligands may in particular be 6-electron donors. The (formally uncomplexed) pincer ligands may be neutral or charged, preferably negatively charged.

Preferably, one, two or all of the pincer ligands of the complex possess the general structures 27, 27a, 28 or 28a in accordance with the formulae below; one, two or all of the pincer ligands of the complex, for example, possess one of the structures 27 or 28, or 27a or 28a. In particular, all the ligands of the complex may possess the structures 27 or 27a or 28 or 28a. It goes without saying that the pincer ligands of a complex may be the same or different. The pincer ligands thus have a central ring with a heteroatom Z or C=atom (carbanion), which binds to the central metal atom, and two further ligand atoms Y, which are linked via bridge atoms or bridging atom groups X to the ring possessing the heteroatom Z. Optionally, one or more of the groups X in the ligands according to the compounds 27, 27a, 28 or 28a may also be missing. The groups X and/or Y within the ligands 27, 27a, 28 or 28a may be the same or different in each case. In particular, the ring carrying the middle ligand atom of the pincer ligands may be a 5-membered or 6-membered ring, which may optionally possess one or more heteroatoms, one of which may be a donor atom. One or both of the X-Y groups in this case may likewise be rings or components of ring systems, especially components of 5 or 6-membered rings, which may in each case possess further heteroatoms in addition to the Y atom. The Y atom may in each case also be a carbon atom. At least one, two or three donor atoms Y, Y' and Z of the pincer ligands or one, two or three or more of the donor atoms of the complex possessing at least two pincer ligands may be different from nitrogen. The pincer ligand may possess at

least one or two or more rings containing one ligand atom in each case with a number of ring atoms different from 6, especially a 5-membered ring. That ring may be the ring containing the middle ligand atom Z, or it may form one of the X-Y groups.

- 5 All the donor atoms may be components of a 5-membered ring, which can in each case be unsaturated or aromatic.





27a

28a

One, two or more donor atoms of the ligands or all the donor atoms of the complex may in each case be components of an aromatic ring or a conjugated, unsaturated system. This applies in particular to donor atoms S, C(II) (carbene), C(carbanion), Si(II) and/or Ge(II). In the case of lower-valent donor atoms, e.g. divalent donor atoms such as carbene, germylene, silylene, the donor atom may in particular also be adjacent to one or two heteroatoms with a free electron pair, such as N, P, As, Ab, S, Se, Te, which is preferably in conjugation with orbitals of the donor atom that are vacant or not maximally occupied. This may apply both to the pincer ligands and also to the monodentate or bidentate ligands mentioned below.

15

In the compounds 27, 27a, 28, 28a, Y is a heteroatom or carbon atom capable of acting as a donor, preferably selected from the group N, P, O, S, Se, Te, C, Si, Ge, Sn, Pb, e.g. selected from the group C, N, P, O, S, Se, though without being restricted to that. The Y atom may be different from N. The two Y atoms may be the same or different. Y may be part of a ring or ring system. In particular, Y may be a carbon atom, e.g. a carbanion or carbene carbon atom, or a Ge atom, in particular a germylene (Ge(II)), or Si atom, especially a silylene (Si(II)), or a sulphur atom.

Z is a heteroatom or carbon atom capable of acting as a donor, preferably selected from the group C, N, P, O, S. If at least one of the Y atoms is an N atom, Z may be different from N. In particular, Z may be a carbon atom, e.g. a carbanion or carbene

carbon atom, or Ge atom, in particular a germylene (Ge(II)), or a Si atom, especially a silylene (Si(II)), or a sulphur atom.

- X is a "spacer" and may be any at least divalent atom or a group of atoms. In particular, X can be a branched or unbranched alkyl chain, in particular a lower alkyl chain with C1 to C6, preferably C1 to C4 or one or two atoms, where X may possess no heteroatoms or one or more heteroatoms. The heteroatoms can be components of the bridge. X can be an aryl substituent, including a condensed aryl substituent with or without heteroatoms, including an alkyl-aryl substituent with or without a heteroatom. X may also be a single heteroatom, such as O, S, N, P or the like. R can be any substituent, preferably H, alkyl, in particular a lower alkyl with C1 to C6, or aryl. The alkyl or aryl residue can be substituted or unsubstituted and may optionally have one or more heteroatoms. The individual substituents R may be the same or different. Two substituents R may be part of a ring, which can be saturated, unsaturated, including aromatic, and may preferably be part of a ring system fused to the skeleton. The statements with regard to R apply to R', R' being in particular an atom other than hydrogen or a group of atoms. The substituents R' may in each case be the same or different from one another.
- E may in each case be an atom selected from the group C, Si, Ge, Sn, Pb, preferably selected from the group C, Si, Ge, in particular C or Ge, for example in oxidation state (II) in each case. The donor atom E may form a carbene, germylene or silylene ligand; preferably, two donor atoms E in each case form a bis-carbene, bis-germylene or bis-silylene ligand or mixed ligands with these donor atoms. The ring of the pincer ligand possessing an E atom preferably has, optionally apart from E, at least one or two further heteroatoms, which are preferably in each case components of a ring, preferably a unsaturated or aromatic ring. The further heteroatom(s) preferably bind(s) to the E atom, optionally via an unsaturated system such as a

double bond. Heteroatoms may in particular be N or S. The ring possessing the donor atom E (in particular as carbene C(II), Ge(II), Si(II)) may have two additional N atoms, two S atoms or one N and one S atom.

5

The complex possessing at least one, more than one or exclusively pincer ligands preferably has at least one central atom selected from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, preferably selected from the group Mn, Fe, Co, Ni, particularly preferably selected from the group Fe, Co, Ni, optionally including Mn. The at least one central atom can be selected from the group Cr, Mo, W, and may, for example, be Mo or W, optionally also Cr. The central atom may also generally be an atom from the 7th to 10th transition metal groups; in this context, it may be different from Cr or Ru, though this is not compulsory.

In particular, compounds 20 to 26 and 29 to 37 may possess the central atoms mentioned above, which may optionally be different from Cr or Ru. The compounds 20 to 26 and 29 to 37 may, however, also possess a different central atom selected from the group of the first, the second or the third transition metal periods.

25

The ligand may be selected from the group of compounds 20 to 24, where one or more of the atoms S or N of the terminal five-membered rings may also be replaced in each case by Se, Te or optionally O, or P, As or Sb. One or more of the double bonds of the five-membered rings of the compounds 20 to 24 may optionally also be saturated. E can in each case be in particular carbene carbon C(II), Ge(II) (germylene) or Si(II) (silylene), optionally also O.

35

The pincer ligand may further be selected from the group of compounds 25 or 26, where the S atom of the middle 5-membered ring or one or both of the S atoms of the terminal 5-membered rings of the compound 26 may be a Se or Te atom, optionally

also O. One or more of the double bonds of the system may also be saturated. It may in each case in particular be carbene carbon C(II), Ge(II) or Si(II).

- 5 For example, the ligand may be selected from the group of compounds 29, 30, 31, where one or more of the S atoms may be replaced by Se or Te, optionally also O, and one or more of the N atoms may be replaced by P, As or Sb. E can in particular be carbene carbon C(II), Ge(II) or Si(II) in each case.

10 The pincer ligand can be selected from the group of compounds 32 to 34, where E may in particular be a divalent C (carbene), Si (silylene) or Ge (germylene) atom. One or more of the N atoms may be replaced by P, As or Sb. One or more of the S atoms may be replaced by Se or Te, or optionally O.

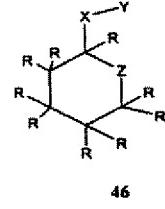
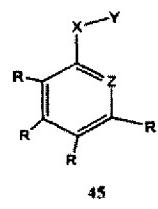
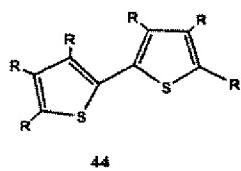
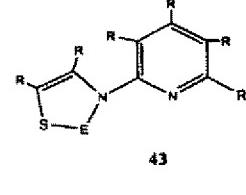
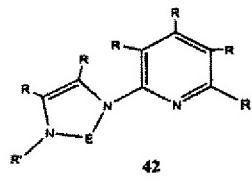
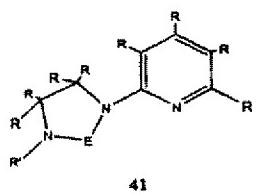
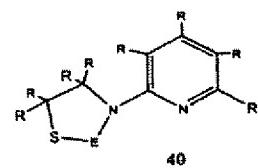
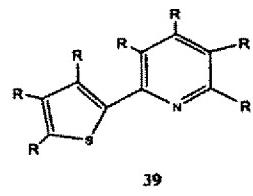
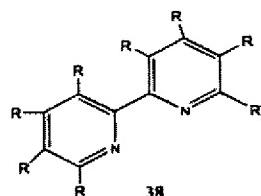
15 The pincer ligand may further be selected from the group of compounds 35, 36 or 37, where E is preferably a divalent carbon atom (carbene), Si(II) or Ge(II). At least one of the N atoms may be replaced by P, As or Sb. At least one of the S atoms may be replaced by Se or Te, or optionally O.

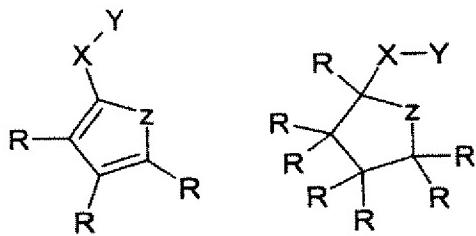
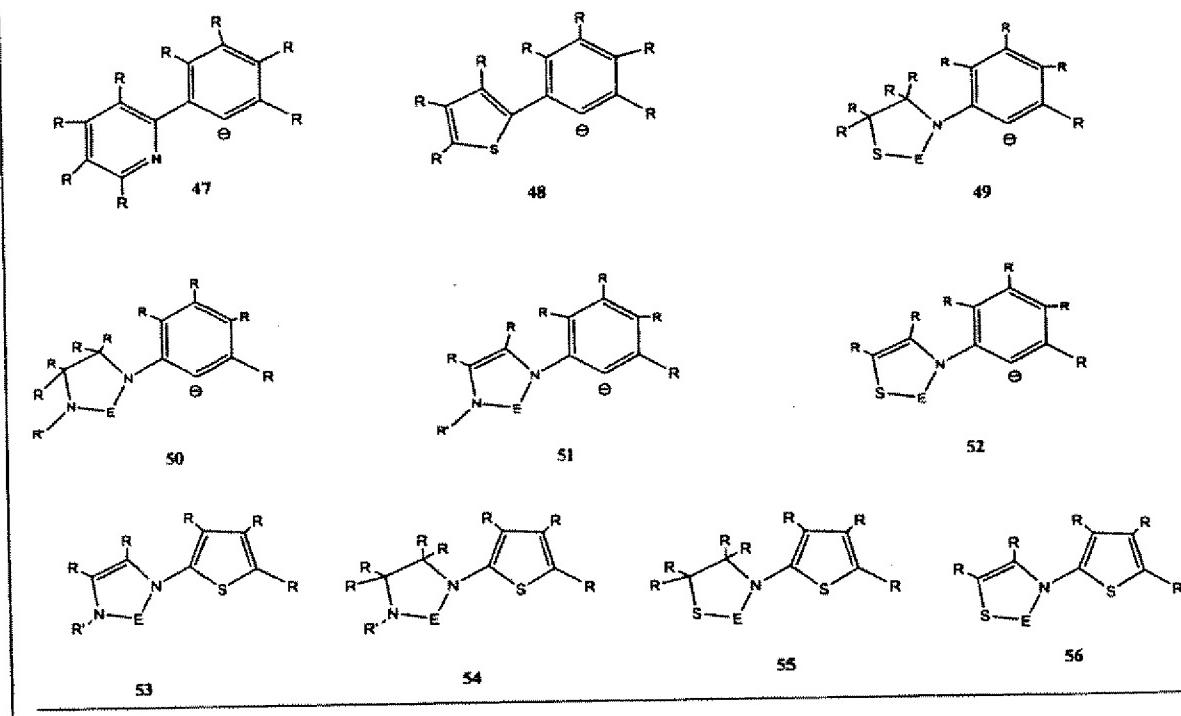
20 If the ligand from the group of compounds 19 to 26 and 29 to 37, in particular the compounds 20 to 26 and 29 to 37, possesses a divalent ligand atom E selected from the group C, Si, Ge, Sn, Pb, in particular selected from the group C, Si, Ge, the central atom of the complex is preferably cobalt, in particular Co (II) or Ru, in particular Ru(0).

25 30 In addition, the ligand may be a bidentate ligand of the general structure 45, 45a, 46, 46a. The X-Y group may in particular form a heterocyclic ring with Y as the hetero donor atom, the ring preferably being a 5 or 6-membered ring. As far as the atoms or groups of atoms Z, X and Y and the substituents R and  
35 R' are concerned, reference may be made to the above comments regarding the pincer ligands.

In particular, one, two or all of the ligands of the complex may be selected from the group of compounds 45, 45a, 46, 46a, such as a compound 45 or 45a or 46 or 46a, with the above statements regarding the pincer ligands applying to the groups 5 Z, X, Y.

In particular, one, two or all of the ligands of the complex may be selected from the group of compounds 38 to 44 and 47 to 10 56, in particular from the group of compounds 39 to 44 and 47 to 56, with the above statements regarding the pincer ligands applying *mutatis mutandis* to the groups R and E. In particular, here too, the ligand may possess a ring with a divalent donor 15 atom S, C, Si, Ge, Sn, Pb, in particular a donor atom C, Si, Ge, so that corresponding carbanions, carbenes, silylenes or germylenes are present.





5 In particular, a ligand with one of the general structures 27,  
 27a, 28, 28a, 45, 45a, 46, 46a may possess a Z atom with C<sup>-</sup>  
 (carbanion) or C(II) (carbene). In particular, one or both of  
 the ligand atoms Y may then be an E atom selected from the  
 group C, Si, Ge, Sn, Pb, in particular selected from the group  
 10 C, Si, Ge, E being divalent (within the ligand).

In particular, the donor atom Y of one of the compounds 27,  
 27a, 28, 28a, 45, 45a, 46, 46a may be the sulphur atom of a  
 thiophene ring which may optionally also be replaced by Se or  
 15 Te, optionally also by O.

In addition, the ligand may be selected from the group of compounds 40, 41, 42, 43, where in each case N may also be replaced by P, As or Sb, and S may in each case be replaced by Se, Te, optionally also O.

5

In addition, the ligand may be selected from the group of compounds 47, 48, 49, 50, 51, 52, in particular also from the group of compounds 49, 50, 51, 52, where in each case S may be replaced by Se or Te or optionally also O, and N may be replaced by P, As, Sb.

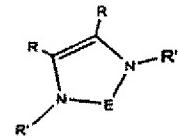
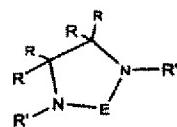
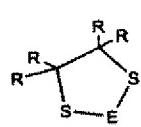
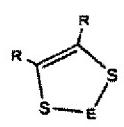
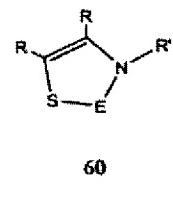
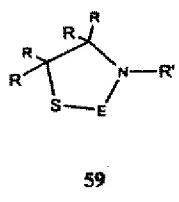
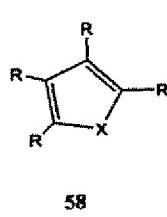
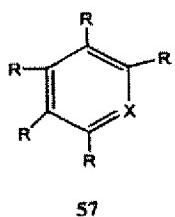
10 The ligand may also be selected from the group of compounds 53, 54, 55 and 56, where S may be replaced by Se, Te or optionally O, and N may be replaced by P, As or Sb, E preferably being C(II) (carbene), Si(II) (silylene) or Ge(II) (germylene).

In addition, at least one, more or all of the ligands may be selected from the group of compounds 57 to 64, in particular selected from the group of compounds 59 to 64, the statements 20 regarding the pincer ligands applying *mutatis mutandis* to E and R, R'. The statements concerning Y or Z with regard to the pincer ligands apply to X as a carbon or hetero donor atom. In particular, the compound 58 may be an, optionally substituted, cyclopentadienyl anion, thiophene, pyrrole, selenophene, phosphene or furan. E is preferably a divalent atom from the group 25 C (carbene), Si (silylene), Ge (germylene), Sn, Pb, preferably selected from the group C, Si, Ge. E can in particular also be C<sup>-</sup> (carbanion). Optionally, one or more double bonds of the compounds 57 to 64 may also be saturated.

30

In compounds of the type 27, 27a and 28, 28a and specifically in the compounds 19 to 26 and 29 to 37, in particular 20 to 26 and 29 to 37, and in the compounds 45, 45a, 46, 46a, specifically in the compounds 38 to 44 and 47 to 56, 39 to 44 and 47 35 to 56, and in the compounds 57 to 64, in particular in the compounds 59 to 64, preferably at least one, more or all of the

rings possessing a donor atom in each case has a hydrocarbon group with 1, 2 or 3 or more, preferably 4 or more carbon atoms, preferably a non-substituted alkyl group or also a substituted alkyl group. The number of C atoms in the group is 5 preferably from 4 to 20 or 4 to 10, inclusive in each case, such as 4 to 6. Preferably, at least one, two or all of the rings are substituted with at least one substituent which exhibits a more powerful +I effect and/or a +M effect vis-à-vis hydrogen or a methyl group. Preferably, at least one, two or 10 all of the donor atoms has/have a +M substituent assigned to it/them which is in conjugation with it/them. Preferably, one, two or more or all of the rings are substituted with at least one alkyl group or a group with the same or a more powerful +I effect. It goes without saying that at least one, more or all 15 of the rings may also possess +M substituents, such as N-alkyl or N-dialkyl substituents (or P instead of N), what has been said above applying to alkyl.



20

It goes without saying that, in the event that at least one or all of the central atoms possess more than one substituent, two or all of the substituents belong to the same substituent type 25 in each case or may be the same.

Ionisation potential/oxidation potential

The metal complex of the invention preferably has an ionisation potential in the gas phase of  $\leq 6.4$  eV, preferably  $\leq 6$  eV, especially  $\leq 5.5$  eV. In particular, the ionisation potential of the complex in the gas phase may be  $\leq 5.0$  eV or  $\leq 4.5$  eV.

5

The gas phase ionisation potential  $I_{pg}$  of the compounds that can be used in accordance with the invention can be determined with reference to tetrathiafulvalene (TTF), for example, which is:  $I_{pg} = 6.4$  eV (see R. Gleiter, E. Schmidt, D. O. Cowan, J P.

10 Ferraris, J. Electr. Spec. Rel. Phenom. 2, 207 (1973)).

The oxidation potential of TTF is  $E_{1/2}(\text{ox}) = -0.09$  V against Fe/Fe<sup>+</sup> (ferrocene/ferrocenium) (M. Iyoda, T. Takano, N. Otani, K. Ugawa, M. Yoshida, H. Matsuyama, Y. Kuwatani, Chem. Lett., 15 1310 (2001)). Proceeding from that point of reference, the redox potential of the n-dopants of the invention against ferrocene/ferrocenium can be  $\leq -0.09$  V, preferably  $\leq -0.6$  V, particularly preferably  $\leq -1.1$  V, such as  $\leq -1.6$  V or  $\leq -2.1$  V, though without being restricted to that.

20

The oxidation potential against ferrocene/ferrocenium can, for example, be determined cyclovoltammetrically. The potential in this case is largely independent of the electrolyte system used and can be determined in accordance with the IUPAC Recommendation (Gritzner, G.; Kuta, J. Pure Appl. Chem. 1984, 56, 461-466). The electrolyte system must have a sufficiently large electrochemical window and the donor compound must be sufficiently soluble. An example of a suitable electrolyte system is acetonitrile / 1M LiClO<sub>4</sub>/Pt electrodes, though other suitable electrolyte systems can also be used.

#### Vapour pressure

The vapour pressure of the complex used in accordance with the invention may in particular be  $< 10^{-3}$  Pa at 30° C, such as  $\leq 5 \times 10^{-4}$  Pa or  $\leq 1 \times 10^{-4}$  Pa.

The n-dopants of the invention used in each case and/or the complexes used in each case may be stable in air; optionally, the n-dopants and/or complexes of the invention used in each case may also be unstable in air.

5

Synthesising the n-dopant complexes of the invention and their ligands

General

- 10 The n-dopant metal complexes of the invention may be synthesised, for example, by synthesising the compounds directly or by reducing salts, the resulting neutral metal complex then being present in the salt as a cation. The anion may be any suitable anion, such as a halogen, perchlorate, sulphate or the like.
- 15 The reduction may be effected electrochemically or chemically for example, though without being restricted to that. The reduction may be effected, for example, by electrocrystallisation, and the product obtained in this way, which can be harvested at the working electrode, can subsequently be purified.
- 20 The complexes of the invention may in particular also be produced without using such an electrocrystallisation step, however.

Synthesis process

- 25 The complexes of the invention can be synthesised using known processes; in some cases, they are also commercially available. The synthesis of the ligands of the complexes of the invention and of the complexes themselves is described in the following passages in the literature for example, each of which is hereby incorporated in the application in full by reference. It goes without saying that the cited passages from the literature are only mentioned by way of example, and that the ligands and complexes can in most cases also be synthesised by other suitable processes.

35

Paddlewheel complexes

The paddlewheel complexes can be isolated either by ligand substitution from other paddlewheel complexes (F. A. Cotton, J. G. Norman Jr., *J. Coord. Chem.* 1 (1970) 161-72; F. A. Cotton, D. J. Timmons, *Polyhedron* 17 (1998) 179-84), by salt metathesis 5 from the metal halide and an anionic ligand (F. A. Cotton, D. J. Timmons, *Polyhedron* 17 (1998) 179-84), by reducing a cationic paddlewheel complex (F. A. Cotton, P. Huang, C. A. Murillo, X. Wang, *Inorg. Chem. Commun.* 6 (2003) 121-6), or in a redox reaction from a metal compound and the ligand (T. A. Stephenson, E. Bannister, G. Wilkinson, *J. Chem. Soc.* (1964) 2538-41).  
10

In addition, a new process has been developed, according to which the paddlewheel complexes of type 65a-d can be isolated efficiently in a single-stage synthesis process. For this purpose, 15 a corresponding inorganic metal salt with free bases of the ligands shown in 65 a-d and a suitable strong reducing agent are heated to reflux in a suitable organic solvent, until the reaction has taken place completely. Suitable solvents to be used are preferably those in which the complexes formed 20 exhibit sufficient stability, though preferably dialkyl ether, cyclic ether, cyclic and open-chain polyether such as 1,4-dioxan, dimethoxyethane, etc., aromatic compounds and mixtures thereof.

Suitable reducing agents are, for example, base metals, preferably 25 alkali metals such as sodium, potassium and caesium.

After separation of the inorganic by-products, the complexes are isolated by crystallisation, precipitation or sublimation.

The novel single-stage synthesis method opens up a time and re-  
30 source-saving access to complexes of the type  $W_2L_4$ .

Some practical embodiments are provided in the following:

Synthesising the ligands and their precursors

1. Imidazo[1,2-a]pyrimidine hydroperchlorate

The production process followed a method described in the literature (M. Künstlinger, E. Breitmaier, Synthesis 1983 (2), 161-162). Deviating from the known method, the product was isolated as imidazo[1,2-a]pyrimidine hydroperchlorate by adding perchloric acid.

10 Fp. 195° C

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN) [ppm]:

8.99-8.96 (m, 2H); 7.98 (d, 1H); 7.93 (d, 1H); 7.58 (dd, 1H)

MS: m/z = 119 [M]<sup>+</sup>

15

2. 5,6,7,8-Tetrahydro-imidazo[1,2-a]pyrimidine

4.2 g imidazo[1,2-a]pyrimidine hydroperchlorate were heated for 8 h in an acetic acid solution with palladium on activated charcoal, with H<sub>2</sub> fed in. Subsequent filtration, removal of the solvent and addition of diethyl ether yielded the 5,6,7,8-tetrahydro-imidazo[1,2-a]pyrimidine hydroacetate in the form of colourless crystals, which were recrystallised from ethanol.

25 Yield: 3.21 g

Fp. 65° C

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:

6.97 (d, 1H); 6.91 (d, 1H); 3.90 (t, 2H); 3.25 (t, 2H); 1.98 (quint., 2H)

30

The 5,6,7,8-tetrahydro-imidazo[1,2-a]pyrimidine was released in an alkaline ethanol solution.

Yield: 3.08 g

35 Fp. 110° C

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:

6.51 (d, 1H); 6.36 (d, 1H); 6.09 (s, 1H); 3.80 (t, 2H); 3.16  
(t, 2H); 1.90 (quint., 2H)  
MS: m/z = 123 [M]<sup>+</sup>

5

*Example 2:*

## 1. 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine

10 1 g 2-amino-4,6-dimethyl pyrimidine was heated for 14 h in a hydrochloric acid environment (2 M HCl) with palladium on activated charcoal as a catalyst, with H<sub>2</sub> fed in. Subsequent filtration, removal of the solvent and addition of diethyl ether yielded the 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine hydrochloride, which was recrystallised from i-propanol/diethyl ether and dried in a vacuum.

Yield: 1.03 g

Fp. 129° C

20 <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:  
8.14 (s, 2H); 6.81 (s, 2H); 3.48 (m, 2H); 1.98 (d, 1H); 1.14  
(d, 6H); 1.10 (d, 1H)

The 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine was released in an alkaline ethanol solution.

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:  
3.46 (m, 2H); 1.98 (m, 1H); 1.13 (d, 6H); 1.10 (d, 1H)

30

## 2. 2,4-dimethyl-3,4-dihydro-2H-pyrimido[1,2-a]pyrimidine hydroperchlorate

35 0.66 g 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine was refluxed to boiling point in a methanolic solution with the addition of perchloric acid with an equimolar amount of 1,1,3,3-

tetramethoxypropane. Removing the solvent and coating the residue with a layer of diethyl ether yielded the 2,4-dimethyl-3,4-dihydro-2*H*-pyrimido[1,2-*a*]pyrimidine hydroperchlorate, which was filtered off and dried in a vacuum.

5

Yield: 0.46 g

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:

9.86 (s, 1H); 8.75 (dd, 1H); 8.55 (dd, 1H); 6.99 (dd, 1H); 4.43 (m, 1H); 3.76 (m, 1H); 2.29 (m, 1H); 1.69 (quar, 1H); 1.57 (d, 3H); 1.27 (d, 3H)

3. 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine

15 0.5 g 2,4-dimethyl-3,4-dihydro-2*H*-pyrimido[1,2-*a*]pyrimidine hydroperchlorate was heated for 8 h in an acetic acid solution with palladium on activated charcoal, with H<sub>2</sub> fed in. Subsequent filtration, removal of the solvent and addition of diethyl ether yielded the 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine hydroacetate in the form of colourless crystals, which were recrystallised from ethanol.

Yield: 0.37 g

Fp. 101° C

25 <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:

7.47 (s, 1H); 7.09 (s, 1H); 3.50-3.55 (m, 1H); 3.43-3.39 (m, 1H); 3.35-3.21 (m, 3H); 3.05-3.03 (m, 1H); 2.11 (m, 1H); 1.95-1.91 (m, 1H); 1.78-1.71 (m, 1H); 1.37-1.30 (quar, 1H); 1.24 (d, 3H); 1.14 (d, 3H)

30

The 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine was released in an alkaline ethanol solution.

Yield: 0.1 g

35 Fp. 133° C

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:

3.24-3.16 (m, 3H); 3.16-3.14 (m, 1H); 3.09-2.93 (m, 1H); 2.86-  
2.83 (m, 1H); 1.89-1.85 (m, 1H); 1.77-1.73 (m, 1H); 1.65-1.58  
(m, 1H); 1.17-1.10 (m, 4H); 0.97 (d, 3H)  
MS: m/z = 167 [M]<sup>+</sup>

5

*Example 3:*

## 1. Benzimidazo[1,2-a]pyrimidine hydroperchlorate

10 The production process followed a method described in the literature (M. Künstlinger, E. Breitmaier, Synthesis 1983 (2), 161-162). Deviating from this, the product was isolated as benzimidazo[1,2-a]pyrimidine hydroperchlorate by adding perchloric acid.

15

Fp. 245° C

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:9.98 (dd, 1H); 9.26 (dd, 1H); 8.60 (d, 1H); 7.95 (d, 1H); 7.86-  
7.81 (m, 2H); 7.73 (t, 1H)

20

## 2. 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine

0.602 g benzimidazo[1,2-a]pyrimidine hydroperchlorate was heated for 9 h in a hydrochloric acid solution (2 M HCl) with palladium on activated charcoal, with H<sub>2</sub> fed in. Subsequent filtration, removal of the solvent and addition of diethyl ether yielded the 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine hydrochloride in the form of colourless crystals, which were recrystallised from ethanol.

30

Yield: 0.18 g

Fp. 212° C

<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:12.62 (s, 1H); 9.18 (s, 1H); 7.47 (m, 1H); 7.38 (m, 1H); 7.27  
(m, 1H); 4.08 (t, 2H); 3.48 (m, 2H); 2.14 (quint., 2H)MS: m/z = 174 [M]<sup>+</sup>

The 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine was released in an alkaline ethanol solution.

Fp. 190° C

5   <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>) [ppm]:  
 7.13-7.07 (m, 3H); 6.92 (m, 1H); 6.85 (m, 1H); 3.96 (t, 2H);  
 3.31 (t, 2H); 2.03 (quint., 2H)  
 MS: m/z = 173 [M]<sup>+</sup>

10

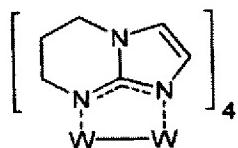
General synthesis of the complexes of the type M<sub>2</sub>L<sub>4</sub>

MCl<sub>4</sub> (WCl<sub>4</sub>, 1.00 g, 3.07 mmol), at least 2 equivalents of the respective ligands (9.21 mmol) and potassium in excess (approx. 1 g) are refluxed in 50 mL THF. It is then allowed to cool and 15 the mother liquor is filtered off. The filtrate is concentrated until dry and extracted with toluene. The product is precipitated with hexane as a brown solid, isolated by filtration and dried in a high vacuum. Yields around 30 %.

20

*Example 4:*

Tetrakis[tetrahydro-imidazo[1,2-a]pyrimidinato]ditungsten-II



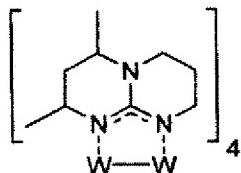
Synthesis as described above with 1.13g of the ligand 5,6,7,8-25 tetrahydro-imidazo[1,2-a]pyrimidine.

<sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) [ppm]:  
 6.7-6.2 (br, 2H); 3.8-3.3 (br, 4H); 1.9-1.3 (br, 2H).

30

*Example 5:*

Tetrakis[dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido-1,2-a]pyrimidinato]ditungsten-II



Synthesis as described above with 1.54 g of the ligand 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidine.

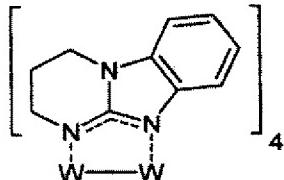
<sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) [ppm]:

- 5 3.5-2.6 (br, 4H); 2.0-1.3 (br, 4H); 1.3-0.9 (br, 6H).  
ESI-MS: m/z = 184 [M<sup>+</sup> + 3 OH].

*Example 6:*

10

Tetrakis[tetrahydro-benzo[4,5]imidazo[1,2-a]pyrimidinato]ditungsten-II



Synthesis as described above with 1.54 g of the ligand 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine.

In a modification of the general synthesis formula, this product is precipitated from the mother liquor with hexane. The solid isolated is not soluble in toluene.

<sup>1</sup>H-NMR (500 MHz, THF-d8) [ppm]:

- 20 6.60 (m, br, 1H); 6.55 (m, br, 1H); 6.40 (m, br, 1H); 6.34 (m, br, 1H); 3.72 (br, 2H); 3.42 (br, 2H); 1.77 (br, 2H).

Carbenes

- 25 Numerous standard procedures are known in the literature for synthesising N-heterocyclic carbenes NHC, namely the imidazole process, the thioketone process and the silver oxide process (metal transfer process). On this subject, see: W. A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290-1309; W. A.

Herrmann, C. Kocher, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 2162-87; A. H. Cowley, *J. Organomet. Chem.* 617-8 (2001) 105-9; T. Westkamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* 600 (2000) 12-22.

5

The thioketone process is based substantially on the principle which is also used for the silylenes and germynes. However, instead of the  $\text{GeCl}_2$  or  $\text{SiCl}_4$ , thiophosgene is used, followed by reduction with potassium, sodium amalgam or  $\text{KC}_8$  (N. Kuhn, T. Kratz, *Synthesis* (1993) 561; F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* 5 (1999) 1931-5).

In the imidazole process, the N-substituted imidazole parent substance is isolated first of all. The second nitrogen atom is then usually quaternised with an alkyl halide, and in the final step, the imidazolium salt is reacted to the carbene with a suitable base ( $\text{KOBu}^t$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{BuLi}$  etc) (see, for example: A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361-3; M. R. Grimmet, *Adv. Heterocyclic Chemistry* 12 (1970) 105 and 134).

20

The silver oxide process is a variant of the imidazole process. In this case, silver oxide is used as the base. A silver complex of the carbene forms. This can transfer the carbene to another metal (metal transfer) (Q.-X. Liu, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Y. L. Chou, Z.-Z. Zhang, *Organometallics* 22 (2003) 309-14; T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay, J. A. C. Clyburne, *Inorg. Chem.* 42 (2003) 1391-3).

30

### Silylenes

The synthesis of the N-heterocyclic silylenes is analogous to that of the corresponding germynes. However, silicon(IV) chloride is used, which means that there must also be a subsequent reduction step (see, for example, M. Denk, R. Lennon, R. Hayshi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* 116 (1994) 2691-2; B.

Gehrhus, M. F. Lappert, J. Organomet. Chem. 617-8 (2001) 209-23).

### Germylenes

- 5 The heterocyclic germylenes (N, S) can usually be isolated by metallising corresponding di-imines, diamines, aminothioles or dithioles and subsequently reacting them with germanium(II) chloride in accordance with known methods (J. Pfeiffer, M. Noltemeyer, A. Meller, Z. Anorg. Allg. Chem. 572 (1989) 145-50; 10 A. Meller, C.-P. Gräbe, Chem. Ber. 118 (1985) 2020-9; J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, Chem. Ber. 122 (1989) 245-52; O. Kühl, P. Lönnecke, J. Heinicke, Polyhedron 20 (2001) 2215-22).
- 15 Synthesising the metal complexes is described, for example, in: O. Kühl, P. Lönnecke, J. Heinicke, Inorg. Chem. 42 (2003) 2836-8; W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, Angew. Chem., Int. Ed. Engl. 31 (1992) 1485.

20

### n perimeter

- In the n perimeter ligands and their metal compounds, there are a large number of compounds and therefore many different methods of synthesising them. The following are mentioned by 25 way of example:

- Cyclopentadienyl: C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 331; J. Okuda, Top. Curr. Chem. 160 (1991) 99; N. J. Coville, K. E. du Plooy, W. Pickl, Coord. Chem. Rev. 116 (1992) 30 1; R. L. Halterman, Chem. Rev. 92 (1992) 965; M. L. Hays, T. P. Hanusa, Adv. Organomet. Chem. 40 (1996) 117; S. Brydges, L. E. Harrington, M. J. McGlinchey, Coord. Chem. Rev. 233-4 (2002) 75; T. Cuenca, P. Royo, Coord. Chem. Rev. 193-5 (1999) 447-98.
- 35 Arenes: A. S. Abd-El-Aziz, Coord. Chem. Rev. 233-4 (2002) 177; A. S. Abd-El-Aziz, Coord. Chem. Rev. 203 (2000) 219; R. D.

Pike, D. A. Sweigart, Coord. Chem. Rev. 187 (1999) 183.

Cycloheptatrienyl: M. L. H. Green, D. P. K. Ng, Chem. Rev. 95 (1995) 439; M. Tamm, B. Dressel, R. Fröhlich, J. Org. Chem. 65 (2000) 6795; M. Tamm, T. Bannenberg, R. Dressel, R. Fröhlich, D. Kunz, Organometallics 20 (2001) 900; M. Tamm, T. Bannenberg, R. Fröhlich, S. Grimme, M. Gerenkamp, Dalton Trans. (2004) 482-91; M. Tamm, B. Dressel, T. Lügger, R. Fröhlich, S. Grimme, Eur. J. Inorg. Chem. (2003) 1088.

10

Cyclo-octatetraenediyl: F. T. Edelmann, D. M. M. Freckmann, H. Schumann, Chem. Rev. 102 (2002) 1851; P. W. Roesky, Eur. J. Inorg. Chem. (2001) 1653.

15 Arene FeCp: these are built up either from the ferrocene by arene substitution and subsequent reduction or by reacting Cp<sup>8</sup>Fe(CO)<sub>2</sub>Br with the arene and subsequent reduction: J.-R. Hamon, D. Astruc, P. Michaud, J. Am. Chem. Soc. 103 (1981) 758-66. Other arene transition-metal-metal Cp complexes can also be 20 isolated accordingly, such as with the metal atoms Mn, Co, Ni, Cu, Zn or even Cr, Mo, W.

#### Borates

Above all, borates in accordance with the compounds 11 to 14 25 and 16 can be produced by means of the following synthesis methods, for example, with other suitable synthesis methods also being possible in each case. It goes without saying that other tripod ligands can optionally also be obtained by means of similar synthesis methods:

30

Building up the pyrazole:

The synthesis is generally effected by reacting a β-diketone with hydrazine: M. B. Smith, J. March, March's Advanced Organic Chemistry, Wiley, New York, 5th edition, 1193

35

Building up the chelate ligand:

According to a first variant, synthesis can be effected by reacting the pyrazole with  $\text{KBH}_4$ , as is described, for example, by S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170

- 5 Alternatively, the chelate ligand can be obtained in a multi-stage synthesis process by reacting boric acid trimethylester and a Grignard compound to isoboronic acid and subsequently reacting it with the pyrazole and pyrazolate: F. R. Bean, J. R. Johnson, J. Am. Chem. Soc. 54 (1932) 4415; E. Khotinsky, M.  
10 Melamed, Chem. Ber. 42 (1909) 3090; H. R. Snyder, J. A. Kuck, J. R. Johnson, J. Am. Chem. Soc. 60 (1938) 105; D. L. Reger, M. E. Tarquini, Inorg. Chem. 21 (1982) 840..

The build-up of the metal complex used in accordance with the  
15 invention is described, for example, in: S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842; C. A. Kilner, E. J. L. McInnes, M. A. Leech, G. S. Beddard, J. A. K. Howard, F. E. Mabbs, D. Collison, A. J. Bridgeman, M. A. Halcrow, Dalton Trans. (2004) 236-43; S. Trofimenko: Scorpionates: The Coordination Chemistry  
20 of Polypyrazolylborate Ligands, Imperial College Press, London 1999; S. Trofimenko, Chem. Rev. 93 (1993) 943; S. Trofimenko, Chem. Rev. 72 (1972) 497; S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170; S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288; A. Paulo, J. D. G. Correia, M. P. C. Campello, I. Santos, Poly-  
25 hedron 23 (2004) 331-60; S. Trofimenko, Polyhedron 23 (2004) 197-203.

Corresponding ligands with a carbon bridge atom instead of boron are obtainable according to C. Pettinari, A. Cingolani,  
30 G. G. Lobbia, F. Marchetti, D. Martini, M. Pellei, R. Pettinari, C. Santini, Polyhedron 23 (2004) 451-69.

Ligands and complexes based on 2-imidazolidine thione can be obtained according to J. K. Voo, C. D. Incarvito, G. P. A. Yap,  
35 A. L. Rheingold, C. G. Riordan, Polyhedron 23 (2004) 405-12; H. M. Alvarez, J. M. Tanski, D. Rabinovich, Polyhedron 23 (2004)

395-403; C. A. Dodds, M. Jagoda, J. Reglinski, M. D. Spicer,  
Polyhedron 23 (2004) 445-50.

Carboranes

5 Building up the carborane system generally requires special conditions. Some representatives are commercially available.

Corresponding synthesis methods are described, for example, by R. A. Wiersboeck, M. F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 10 1642-3; J. A. Dupont, M. F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 1643; L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, B. N. Storhoff, Inorg. Chem. 9 (1970) 2175-9.

The synthesis of the corresponding metal complexes has been described, for example, by J. Bould, John D. Kennedy, G. Ferguson, F. T. Deeney, G. M. O'Riordan, T. R. Spalding, Dalton Trans. (2003) 4557-64.

Triazacycloalkanes

20 The substituents at the nitrogen atom can be isolated by alkylation or arylation from the trisammonium bromide of the parent substance. They are subsequently reacted with metal precursors. See, for example: R. Zhou, C. Wang, Y. Hu, T. C. Flood, Organometallics 16 (1997) 434; L. Wang, C. Wang, R. Bau, T. C. Flood, 25 Organometallics 15 (1996) 491; L. Wang, J. R. Sowa Jr., C. Wang, R. S. Lu, P. G. Gasman, T. C. Flood, Organometallics 15 (1996) 4240; S. M. Yang, M. C. W. Chan, K. K. Cheung, C. M. Che, S. M. Peng, Organometallics 16 (1997) 2819; S. M. Yang, W. C. Cheng, S. M. Peng, K. K. Cheung, C. M. Che, Dalton Trans (1995) 2955; A. L. Gott, P. C. McGowan, T. J. Podesta, C. W. Tate, Inorg. Chim. Acta 357 (2004) 689-98.

Tripod ligands

35 The tripod ligand class of compounds is also characterised by its wide variety. Some synthesis methods regarding compounds to be used in accordance with the invention have been described

by:

Carbene-based ligands, in particular with a carbene donor atom:  
H. Nakai, Y. Tang, P. Gantzel, K. Meyer, *Chem. Comm.* (2003) 24-  
5 5; X. Hu, I. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* 125  
(2003) 12237-45; U. Kernbach, M. Ramm, P. Luger, W. P. Fehl-  
hammer, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 310-2;

Nitrogen-based ligands, in particular with an N donor atom: T.  
10 Rüther, N. Braussaud, K. J. Cavell, *Organometallics* 20 (2001)  
1247-50; L. Peters, N. Burzlaff, *Polyhedron* 23 (2004) 245-51;  
V. V. Karambelkar, R. C. diTargiani, C. D. Incarvito, L. N.  
Zakharov, A. L. Rheingold, C. L. Stern, D. P. Goldberg, *Poly-  
hedron* 23 (2004) 471-80; D. L. Reger, J. R. Gardiner, M. D.  
15 Smith, *Polyhedron* 23 (2004) 291-9; M. Scarpellini, J. C. Toledo  
Jr., A. Neves, J. Ellena, E. E. Castellano, D. W. Franco,  
*Inorg. Chim. Acta* 357 (2004) 707-15;

Phosphorus-based ligands, in particular with a P donor atom: H.  
20 A. Mayer, W. C. Kaska, *Chem. Rev.* 94 (1994) 1239; B. C. Jans-  
sen, A. Asam, G. Huttner, V. Sernau, L. Zsolnai, *Chem. Ber.* 127  
(1994) 501; H. Heidel, J. Scherer, A. Asam, G. Huttner, O.  
Walter, L. Zsolnai, *Chem. Ber.* 128 (1995) 293; S. Beyreuther,  
J. Hunger, G. Huttner, S. Mann, L. Zsolnai, *Chem. Ber.* 129  
25 (1996) 745; J. C. Thomas, J. C. Peters, *Polyhedron* 23 (2004)  
489-97.

Sulphur-based ligands, in particular with an S donor atom: H.  
M. Alvarez, J. M. Tanski, D. Rabinovich, *Polyhedron* 23 (2004)  
30 395-403.

The preparation of metallotriphos ligands that can be used in  
accordance with the invention has been described by: O. Kühl,  
S. Blaurock, J. Sieler E. Hey-Hawkins, *Polyhedron* 20 (2001)  
35 2171-7; G. S. Ferguson, P. T. Wolczanski, L. Parkanyi, M. C.  
Zonneville, *Organometallics* 7 (1988) 1967; S. M. Baxter, G. S.

Ferguson, P. T. Wolczanski, J. Am. Chem. Soc. 110 (1988) 4231.

Fullerenes

In general, it is possible to proceed in a similar way to the  
5 cyclopentadienyl ligands, though without wishing to be re-  
stricted to that. For this purpose, the metallated species can  
be reacted with a metal precursor. See, for example: L. A.  
Rivera-Rivera, G. Crespo-Roman, D. Acevedo-Acevedo, Y. Ocasio-  
Delgado, J. E. Cortes-Figueroa, Inorg. Chim. Acta 357 (2004)  
10 881-7.

Pincer ligands

Regarding the synthesis of pincer ligands that can be used in  
metal complexes of the invention, see, for example: A. M.  
15 Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V.  
C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W.  
Skelton, J. Organomet. Chem. 617-8 (2001) 546-60.

Carbene-based pincer ligands: The ligand system can be synthe-  
20 sised by high-temperature synthesis from 2,6-dibromopyridine  
and N-substituted imidazole: R. S. Simons, P. Custer, C. A.  
Tessier, W. J. Youngs, Organometallics 22 (2003) 1979-82; J. A.  
Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H.  
Crabtree, Organometallics 21 (2002) 700; M. Poyatos, J. A.  
25 Mata, E. Falomir, R. H. Crabtree, E. Peris, Organometallics 22  
(2003) 1110-4; A. A. D. Tulloch, A. A. Danopoulos, S. Winston,  
S. Kleinhenz, G. Eastham, Dalton Trans (2000) 4499; A. A.  
Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham, M. B.  
Hursthouse, Dalton Trans (2003) 1009-15.

30 Phosphorus-based pincer ligands, in particular with a P donor  
atom, can be isolated from an alpha,alpha'-xylene- or lutidine  
dihalide by salt metathesis with a secondary phosphanide, for  
example according to W. V. Dahlhoff, S. M. Nelson, J. Chem. Soc  
35 (A) (1971) 2184; L. Barloy, S. Y. Ku, J. A. Osborn, A. DeCian,  
J. Fisher, Polyhedron 16 (1997) 291; B. D. Steffey, A. Mie-

damer, M. L. Maciejewski-Farmer, P. R. Bernatis, A. M. Herring, V. S. Allured, V. Caperos, D. L. DuBois, *Organometallics* 13 (1994) 4844; C. Hahn, A. Vitagliano, F. Giordano, R. Taube, *Organometallics* 17 (1998) 2060; G. Vasapollo, C. F. Nobile, A. Sacco, *J. Organomet. Chem.* 296 (1985) 435-41; G. Jin, H. M. Lee, I. D. William, *J. Organomet. Chem.* 534 (1997) 173; G. Jin, H. M. Lee, H. P. Xin, I. D. William, *Organometallics* 15 (1996) 5453; T. Karlen, P. Dani, D. M. Grove, P. Steenwinkel, G. Van Koten, *Organometallics* 15 (1996) 5687;

10

#### Bidentate ligands

Biscarbenes with carbene donor atoms which can be used in accordance with the invention can be prepared according to M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* 42 (2003) 2572-6. The synthesis follows the literature citations already described above.

#### Monodentate ligands

The synthesis can follow the literature citations already described above. Ligands of this kind are in some cases also available commercially.

#### Matrix materials

In the present invention, suitable n-dopants for organic semiconducting materials such as electron transport materials are described, e.g. those generally used in electronic devices, including optoelectronic devices, such as OLEDs, field effect transistors or organic solar cells. The semiconducting materials are preferably intrinsically electron-conductive.

30

The matrix material may consist partially (> 10 or > 25 % by weight) or substantially (> 50 % by weight or > 75 % by weight) or completely of a metal phthalocyanine complex, a Buckminster fullerene, optionally also a porphyrin complex, especially a metal porphyrin complex, an oligothiophene, oligophenyl, oligophenylene vinylene or oligofluorene compound, the oligomers

preferably comprising 2-500 or more, preferably 2-100 or 2-50 or 2-10 monomeric units. The oligomer may also comprise > 4, > 6 or > 10 or more monomeric units, especially also for the ranges specified above, i.e., for example, 4 or 6-10 monomeric  
5 units, 6 or 10-100 monomeric units or 10-500 monomeric units. The monomers or oligomers can be substituted or unsubstituted, and block or mixed polymers from the oligomers mentioned may also be present. The matrix can also be a mixture of oligomers with various chain lengths, as is the case for standard polymer  
10 layers.

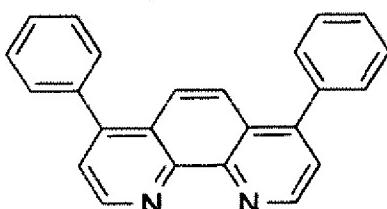
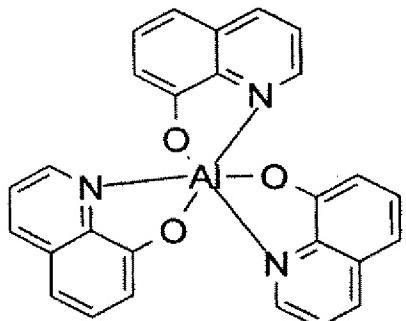
The matrix material may also be a compound with a triarylamine unit or spiro-bifluorene compound. The matrix materials mentioned may also be present in combination with one another,  
15 optionally also in combination with other matrix materials. The matrix materials may possess electron-pushing substituents such as alkyl or alkoxy residues which have reduced ionisation energy or which reduce the ionisation energy of the matrix material.

20 The metal phthalocyanine complexes or porphyrin complexes used as the matrix material may have a metal atom from the main group or the B group. The metal atom Me may in each case be 4, 5 or 6-fold co-ordinated, such as in the form of oxo ( $\text{Me}=\text{O}$ ),  
25 dioxo ( $\text{O}=\text{Me}=\text{O}$ ), imine, di-imine, hydroxo, dihydroxo, amino or diamino complexes, though without being restricted to those. The phthalocyanine complex or porphyrin complex may in each case be partially hydrogenated, though the mesomeric ring system is preferably not disturbed in the process. As the central  
30 atom, the phthalocyanine complexes may, for example, contain magnesium, zinc, iron, nickel, cobalt, magnesium, copper or vanadium oxide (= VO). The same or other metal atoms, or oxo-metal atoms may be present in the case of porphyrin complexes.

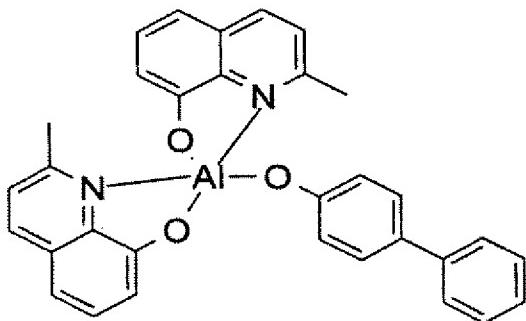
35 The following may also be used as n-dopable matrix materials: quinolinato complexes, such as those of aluminium or other met-

als from the main group, it also being possible for the quinolinato ligand to be substituted. In particular, the matrix material may be tris(8-hydroxy-quinolinato)-aluminium. Other aluminium complexes with O and/or N donor atoms can optionally

5 also be used.



tris (8-hdroxy-quinolinato)-aluminium      BPhen= bathophenanthroline  
 (4,7-Diphenyl-1,10-phenanthroline)  
 C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>



10      Bis-(2-methyl-8-quinolinolato)-4-(phenyl-phenolato)-aluminium-(III)

The quinolinato complexes may, for example, contain one, two or three quinolinato ligands, the other ligands preferably complexing to the central atom with O and/or N-donor atoms, such

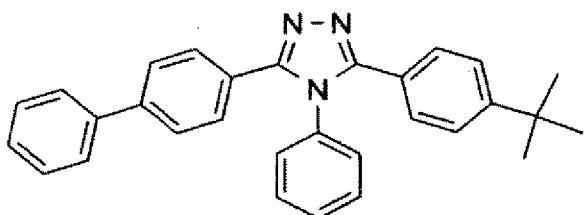
15 as the above Al complex, for example.

Phenanthrolines, which may be substituted or unsubstituted, can also be used as matrix materials, in particular aryl-substituted, such as phenyl or naphthyl-substituted. In particular,

Bphen can be used as the matrix material.

Heteroaromatic compounds can also be used as matrix materials, such as in particular triazoles, optionally also pyrroles, imidazoles, triazoles, pyridines, pyrimidines, pyridazines and the like. The heteroaromatic compounds are preferably substituted, in particular aryl-substituted, such as phenyl or naphthyl-substituted. In particular, the triazole shown below can be used as the matrix material.

10.



3-(4-Biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole

C<sub>30</sub>H<sub>27</sub>N<sub>3</sub>

The matrix material used preferably consists completely of a metal phthalocyanine complex, in particular ZnPc, a porphyrin complex, or a Buckminster fullerene, in particular fullerene C<sub>60</sub>.

It goes without saying that the matrix materials mentioned can also be used mixed with each other or with other materials in the context of the invention. It goes without saying that other suitable organic matrix materials can also be used if they possess semiconducting properties.

#### Doping concentration

25 The invention further relates to an organic semiconducting material containing a metal complex of the invention as an n-dopant. The dopant is preferably present in a doping concentra-

tion of ≤ 1:1 relative to the matrix molecule, or the monomeric unit of a polymeric matrix molecule, preferably in a doping concentration of 1:2 or less, particularly preferably 1:5 or less or 1:10 or less. The doping concentration may lie in the 5 region of 1:1 to 1:100,000 or less, especially in the region of 1:5 to 10,000 or 1:10 to 1,000, such as in the region of 1:10 to 1:100 or 1:25 to 1:50, though without being restricted to that.

10 Performing the doping

The doping of the respective matrix material with the n-dopant to be used in accordance with the invention can be achieved by means of one or a combination of the following processes:

- 15      a) Mixed vaporisation in a vacuum with one source for the matrix material and one for the dopant.
- b) Sequential deposition of the matrix material and the n-dopant on a substrate, subsequently diffusing the dopant in, in particular by means of thermal treatment
- 20      c) Doping a matrix layer using a solution of n-dopant, followed by evaporating the solvent, in particular by means of thermal treatment
- d) Surface-doping a layer of matrix material by means of a layer of dopant applied to the surface
- 25      e) Preparing a solution of matrix molecules and dopant and then preparing a layer of this solution by conventional methods, such as evaporating the solvent or hydro-extracting
- 30      The doping may optionally also take the form of evaporating the dopant out of a precursor compound, which is released when the dopant is heated and/or irradiated. As the precursor compound, it is possible in each case to use a carbonyl compound, di-nitrogen compound or the like, which cleave off CO, nitrogen or 35 the like when the dopant is released, though other suitable precursors can also be used, such as salts, e.g. halides or the

like. Irradiation can be performed by means of electromagnetic radiation, especially visible light, UV light or IR light, such as laser light in each case, or also by other types of radiation. The irradiation is able to provide substantially all the  
5 heat needed for vaporisation; it is also possible to irradiate in a targeted manner into specific bands of the compounds, precursors or compound complexes, such as charge-transfer complexes, in order, for example, by transferring them into excited states, to facilitate the vaporisation of the compounds by dissociation of the complexes. The complex may, however, in particular also be sufficiently stable, to evaporate under the given conditions without dissociation or to be applied to the substrate. It goes without saying that other suitable processes for carrying out the doping can also be used.

15 n-doped layers of organic semiconductors in accordance with the invention, which are suitable for a wide variety of uses, can thus be prepared in this way.

20 Semiconducting layer

With the metal complexes used in accordance with the invention, semiconducting layers can be produced which may optionally also be linear in shape, such as conductivity paths, contacts or the like. The metal complexes may in this case be used as n-dopants  
25 together with another compound, which can act as the matrix material, with the doping ratio being 1 : 1 or less. The metal complex used in accordance with the invention may be present to the other compound or component in each case, but also in higher proportions, so that the ratio of metal complex : compound  
30 may be in a ratio of > 1 : 1, such as in a ratio of ≥ 2 : 1, ≥ 5 : 1, ≥ 10 : 1 or ≥ 20 : 1 or higher. The other component in each case may be one of the kind that can be used as the matrix material in the case of preparing doped layers, though without being restricted to this. The metal complex used in accordance  
35 with the invention may optionally also be present in substantially pure form, such as in the form of a pure layer.

The region containing a metal complex of the invention or consisting substantially or completely of said metal complex may in particular be contacted in an electrically conductive manner with an organic semiconducting material and/or an inorganic 5 semiconducting material; it may, for example, be arranged on a substrate of this kind.

In accordance with the invention, the metal complexes mentioned are preferably used as n-dopants, e.g. in a ratio of  $\leq 1 : 1$  or 10  $\leq 1 : 2$ , or as explained earlier on. With the metal complexes used as n-dopants in accordance with the invention, it is possible, for example, when fullerene C<sub>60</sub> is used as the matrix, to obtain semiconducting layers with conductivities at room temperature in the region of 10<sup>-5</sup> S/cm or higher, for example 15 10<sup>-3</sup> S/cm or higher, e.g. 10<sup>-1</sup> S/cm. When phthalocyanine zinc was used as the matrix, a conductivity of higher than 10<sup>-8</sup> S/cm was obtained, for example 10<sup>-6</sup> S/cm. So far, it has not been possible to dope this matrix with organic donors, because the reduction potential of the matrix is too low. The conductivity 20 of undoped phthalocyanine zinc, on the other hand, is a maximum of 10<sup>-10</sup> S/cm.

It goes without saying that the layer or the structure with a metal complex in accordance with the invention may in each case 25 contain one or more different complexes of this kind.

#### Electronic device

Using the organic compounds of the invention to prepare n-doped organic semiconducting materials, which can be arranged in particular in the form of layers or electrical line paths, a wide 30 variety of electronic devices or devices containing them can be produced with an n-doped organic semiconductor layer, which are thus also encompassed by the invention. For the purposes of the invention, the term "electronic devices" also comprises opto-electronic devices. With the compounds of the invention, the 35 electronic characteristics of an electronically functionally

effective aspect of the device, such as its electrical conductivity, light-emitting characteristics or the like, can be changed advantageously. Using the metal complexes of the invention as n-dopants, for example, it is possible to improve 5 the conductivity of the doped layers and/or the injection of the charge carriers of contacts into the doped layer.

The invention encompasses in particular organic light-emitting diodes (OLED), organic solar cells, organic diodes, especially 10 those with a high rectification ratio, such as  $10^3$ - $10^7$ , preferably  $10^4$ - $10^7$  or  $10^5$ - $10^7$ , and organic field effect transistors which are produced using the neutral metal complexes of the invention.

15 In the electronic device, an n-doped layer in accordance with the invention, based on an organic matrix material, may be present in the following layer structures, for example, the base materials or matrix materials of the individual layers preferably being organic in each case:

20 M-i-n: metal-isolator-n-doped semiconductor, where the M layer forms the metal base contact and may, for example, be ITO, Au, Ag, Al etc. The top contact forms an ohmic contact with the n-doped layer and may consist, for example, of Al. The "i" layer 25 stands for an undoped layer.

n-i-M: what has been said regarding the M-i-n structure applies; the difference with regard to the latter, however, is that the ohmic contact is provided on the substrate.

30 p-i-n: p-doped semiconductor-isolator-n-doped semiconductor,  
n-i-p: n-doped semiconductor-isolator-p-doped semiconductor,  
"i" is once again an undoped layer, "p" is a p-doped layer. The contact materials here are hole-injecting - in this case, a 35 layer or contact of ITO or Au may be provided on the p-side for example -, or electron-injecting - in this case, a layer or

contact of ITO, Al or Ag may be provided on the n-side.

In the above structures, the i-layer may also be omitted if need be, as a result of which sequences of layers with p-n or 5 n-p transitions can be obtained.

The use of the dopant of the invention is not, however, limited to the above-mentioned embodiments; in particular, the layer structures can be supplemented or modified by introducing additional appropriate layers. In particular, OLEDs with sequences 10 of layers of this kind can be built up in each case, in particular with a p-i-n structure or one inverse thereto, with n-dopants of the invention.

15 With the help of the n-dopants of the invention, organic diodes of the metal-isolator-n-doped semiconductor type (m-i-n) in particular - or also optionally of the p-i-n type - can be produced, for example on the basis of phthalocyanine zinc. These diodes exhibit a rectification ratio of  $10^5$  and higher. In addition, using the dopants of the invention, electronic devices 20 with p-n transitions can be produced, in which the same semiconducting material is used for the p as for the n-doped side in each case (homo-p-n transition) and in which a metal complex in accordance with the invention is used for the n-doped semi-25 conducting material. Components of this kind are thus also encompassed by the invention.

The metal complexes may be used in accordance with the invention in the electronic devices, but also in layers, conductivity paths, point contacts or the like if the latter predominate 30 over other components, for example as an injection layer in a pure or substantially pure form.

#### Practical embodiments

35 An electron-rich neutral metal complex in accordance with the invention is provided, wherein the metal complex may in each

case be, for example:

M-to-(terpyridine) with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2hpp_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(AlkylCOO)_4$ ; F with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W and with alkyl in each case, the same as each other or different from one another, with Cl to ClO;  $M_2(guanidinate)_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(formamidinate)_4$ , with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(carboxylate)_4$ , with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(halide)_4$ , with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; bis( $\eta^5$ -cyclopentadienyl)-M with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; benzene-M-( $\eta^5$ -cyclopentadienyl) with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; Fe(ligand)<sub>2</sub>, wherein the ligand may be one of the compounds 20 to 37 with E = -C- or -Ge- or -Si-, at least one R, more than one or all R preferably being hydrogen or methyl or ethyl in each case. Instead of Fe, the central atom can also in particular be Cr, Mn, Co, Ni, Cu or Zn or Mo or W in each case. In addition, the compounds 21, 22, 23, 24 in particular can be used, where R is hydrogen or methyl. E can in this case be -C- or -Ge- in particular, as a result of which the corresponding biscarbene ligands or bisgermylene ligands are present. It goes without saying that optionally one or more of the hydrogen atoms of the ligands may be replaced by other residues, including alkyl residues.

It is also possible, for example, for a metal complex according to one of the compounds 11 to 14, 16 to be prepared, where R and R'' are methyl in each case and E is S in each case. The central atom is Fe. Alternatively, the central atom in each case is Cr, Mn, Co, Ni, Cu, Zn or Mo or W.

Once prepared, the metal complex is vaporised simultaneously with the matrix material. According to the embodiment, the matrix material in each case is phthalocyanine zinc or fullerene C<sub>60</sub>. The N-dopant and matrix material can be vaporised in such

a way that the layer deposited on a substrate in a vacuum evaporation unit has a doping ratio of n-dopant to matrix material of 1:10.

- 5 The layer of the organic semiconducting material doped in each case with the n-dopants of the invention is applied to an ITO layer (indium tin oxide), which is arranged on a glass substrate. After the n-doped organic semiconductor layer of the invention has been applied, a metal cathode is applied, for  
10 example by vapour-deposition of a suitable metal, in order to produce an organic light-emitting diode. It goes without saying that the organic light-emitting diode can also have a so-called inverted layer structure, the sequence of layers being: glass substrate - metal cathode -n-doped organic layer - transparent  
15 conductive top layer (for example ITO). It goes without saying that, depending on the particular application, further layers may be provided between the individual layers mentioned.

Example 1:

- 20 The neutral cobalt complex cobalt-bis(phenylene-1-yl-2,6 dipyridyl) (ligand: compound 29) was prepared using a conventional process.

The neutral complex was sealed in ampoules under a protective gas. With oxygen excluded, a vaporiser source was then filled with this material. Doped layers with a dopant : matrix material doping ratio of 1 : 10 were prepared by the mixed evaporation of the matrix and dopant with ZnPc as the matrix material. In thin-film field effect transistors with a ZnPc layer doped  
30 in this way, an increase in the source-drain current for a positive gate voltage was found. This proves the presence of electrons as the majority charge carriers in the ZnPc layer. In this way, it was shown that it is indeed an n-doped semiconducting material.

35

The same may also apply, *mutatis mutandis*, to the Ruthenium

complex Ru-bis-(pyridine-2,6-di-(1H2H-N-imidazolyl-)) (ligand: compound 23 with E = -C-).

Example 2:

5 A layer of zinc phthalocyanine (ZnPc) was doped with the metal complex [Cr<sub>2</sub>(hpp)<sub>4</sub>]. The doped layer was produced by mixed evaporation of the ZnPc matrix and the dopant Cr<sub>2</sub>(hpp)<sub>4</sub> in a high vacuum. The concentration of the dopant in the matrix was 1.9 mol %. The sublimation temperature of the dopant was  
10 160° C. The doped layer exhibited a high conductivity of 4x10<sup>-6</sup> S/cm. By curing the layer at 70° C, it was possible to increase the conductivity to 6x10<sup>-5</sup> S/cm. The activation energy of the conductivity was 0.27 eV.

15 Example 3:

A layer of fullerene C<sub>60</sub> was doped with the metal complex cobaltocene. First of all, a pure layer of the fullerene was produced by sublimation in a high vacuum. That layer had a low conductivity of 1x10<sup>-7</sup> S/cm. The doped layer was then placed in  
20 a container in which there was a vaporiser filled with cobaltocene. The container was filled with nitrogen. The cobaltocene was sublimed thermally in that container. The cobaltocene deposited on the surface of the fullerene layer led to the formation there of a thin highly doped layer. The cross-current measured in the layer increased by 3 orders of magnitude in the process. The conductivity of the highly doped layer was therefore at least 1x10<sup>-4</sup> S/cm. The fullerene layer doped in this way was then transferred back to the vacuum chamber. There,  
25 high conductivities of at least 2x10<sup>-5</sup> S/cm continued to be measured. In this way, it was proven that the increase in conductivity observed was indeed due to the doping of the fullerene, since any layers of pure, neutral cobaltocene that might be formed are not stable, because of their vapour pressure in  
30 the high vacuum.

Claims

1. Use of a metal complex as a dopant for doping an organic semiconducting matrix material in order to alter the latter's electrical characteristics, wherein the metal complex constitutes an n-dopant with regard to the matrix material, or the use of a metal complex to produce an electronic device with an electronically functionally effective region containing the metal complex, characterised in that the metal complex is a neutral electron-rich metal complex.  
5
2. The use as claimed in claim 1, characterised in that the central atom is a neutral or charged transition metal atom.  
15
3. The use as claimed in either of claims 1 or 2, characterised in that at least one central atom of the complex has a formal number of valence electrons of 16 or more and/or that the complex is polynuclear and has at least one metal-metal bond between two metal central atoms of the complex.  
20
4. The use as claimed in any of claims 1 to 3, characterised in that at least one donor atom of the ligand binding to the central atom is different from an aromatic nitrogen atom as a component of a 6-membered ring.  
25
5. The use as claimed in any of claims 1 to 4, characterised in that at least one, more or all of the donor atoms binding to the central atom are selected from the group consisting of B, Al, Ga, In, C, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te.  
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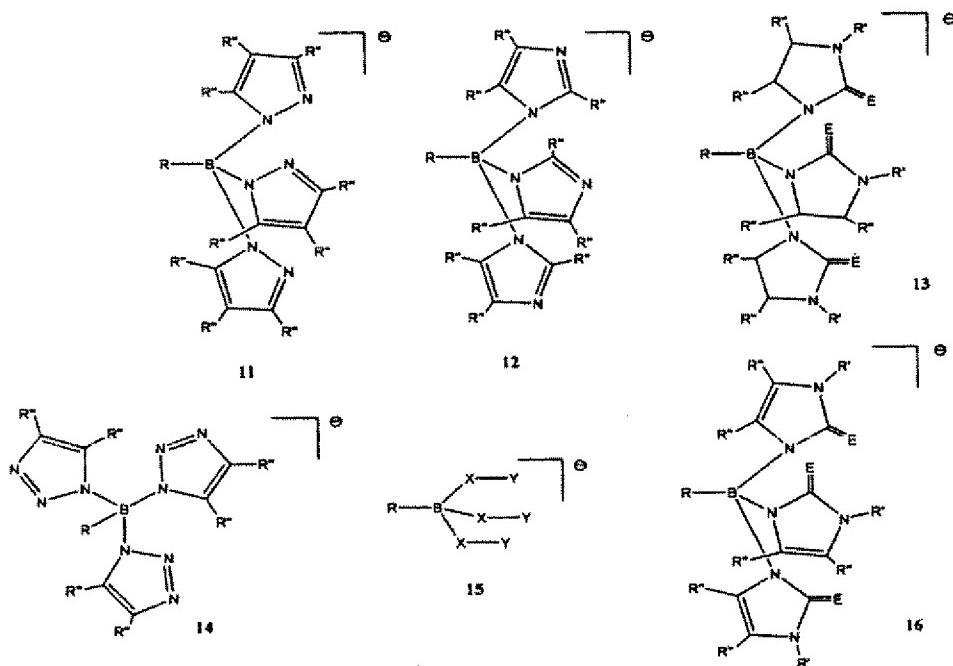
6. The use as claimed in any of claims 1 to 5, characterised in that at least one ligand forms a n complex with the central atom.

5 7. The use as claimed in any of claims 1 to 6, characterised in that the metal complex is a poly-nuclear metal complex in which at least one, more or all of the ligands in each case co-ordinate to at least two metal central atoms.

10 8. The use as claimed in any of claims 1 to 7, characterised in that at least one or all of the ligands of the complex are selected from the group of halides, carboxylates, formamidinates, pyrimido-pyrimidines, hpp and guanidinates.

15 9. The use as claimed in any of claims 1 to 8, characterised in that at least one ligand belongs to the class of compounds of borates, carboranes, triazacycloalkanes, triazacycloalkenes, pyrroles, thiophenes, 20 pyrazoles, imidazoles, thiazoles, oxazoles or fullerenes.

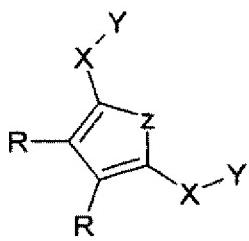
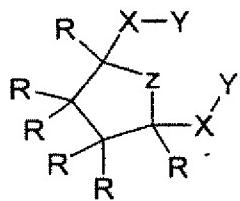
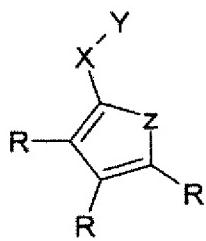
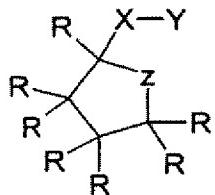
25 10. The use as claimed in claim 9, characterised in that at least one borate ligand is one of the following compounds 11, 12, 13, 14, 16, where R, R' and R'', independently of one another, are any substituent, including hydrogen, and R, R' and R'' can be the same or different in each case, and E is an at least divalent atom or group of atoms:



- 5 11. The use as claimed in any of claims 1 to 10, characterised in that at least one donor atom binding to the at least one metal central atom is a carbanion-carbon atom or, with regard to the ligand, a formally divalent atom selected from the group of C (carbene), Si (silylene), Ge (germylene), Sn, Pb.

10 12. The use as claimed in claim 11, characterised in that the ligand has at least one or two donor atoms binding to the at least one metal central atom as carbanion-carbon atoms or, with regard to the ligand, a formally divalent atom selected from the group of C (carbene), Si (silylene), Ge (germylene), which are in each case components of an aromatic or non-aromatic ring, and that the ring possessing the donor atom possesses a further heteroatom, which is N, P, As, S, Se or Te.

15 13. The use as claimed in any of claims 1 to 12, characterised in that at least one ligand is a compound of the formula 27, 27a, 28, 28a, 45, 45a, 46 or 46a

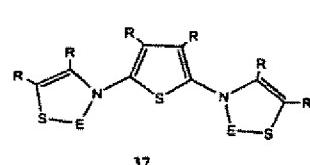
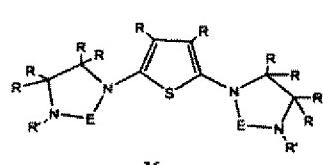
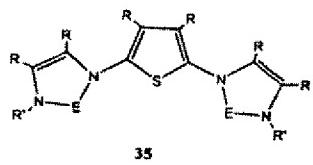
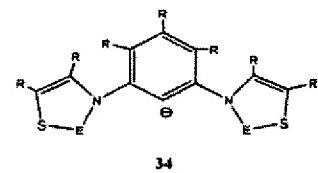
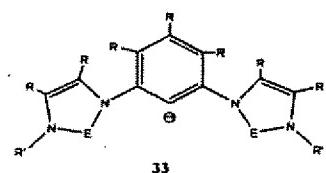
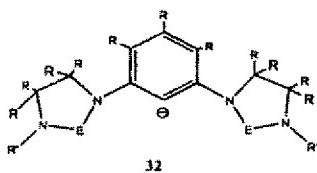
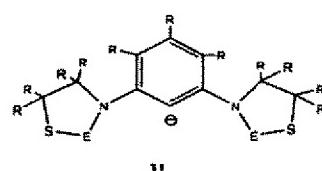
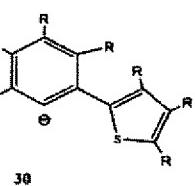
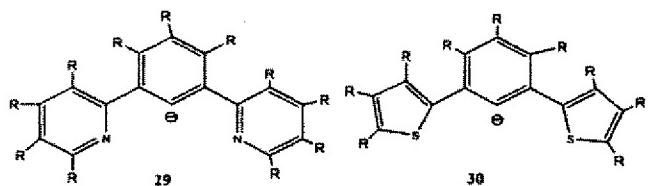
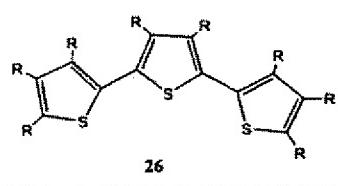
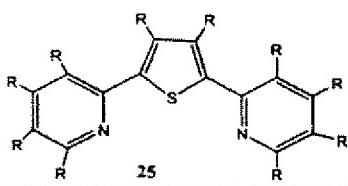
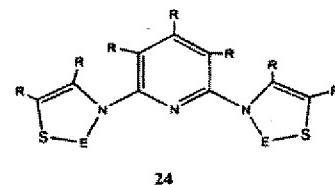
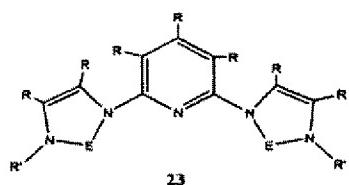
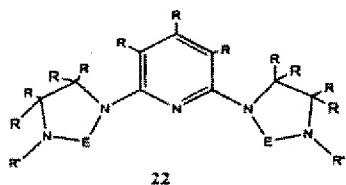
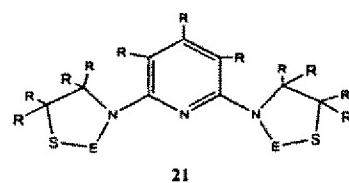
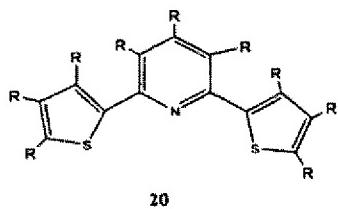
**27a****28a****45a****46a**

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where R is, in each case and independently of one another, any substituent, including hydrogen, X is a heteroatom or carbon atom capable of acting as a donor, X is an at least 10 divalent atom or group of atoms, where one or two X may optionally also be missing, and Z and Y are in each case a carbon or heteroatom capable of acting as a donor, where Z and Y and two Y atoms can be the same as one another or different from one another in each case.

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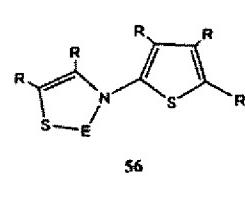
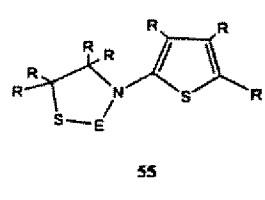
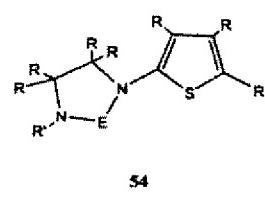
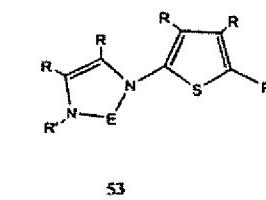
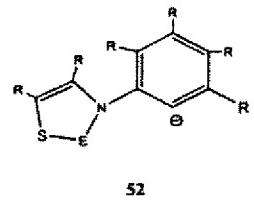
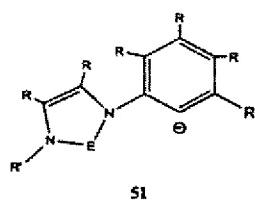
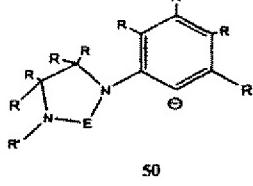
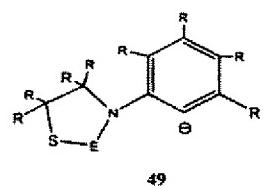
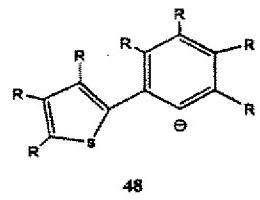
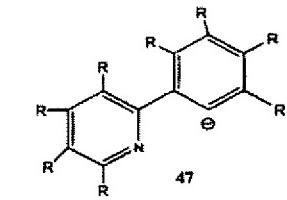
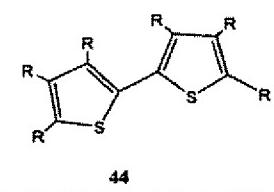
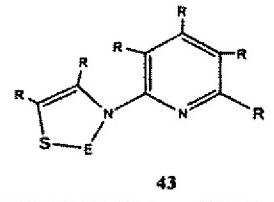
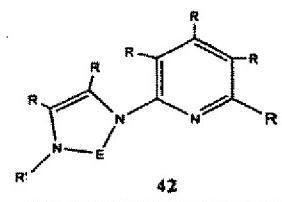
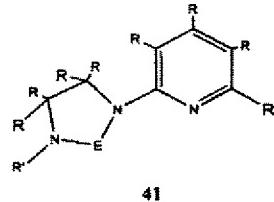
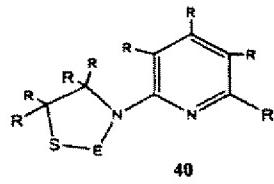
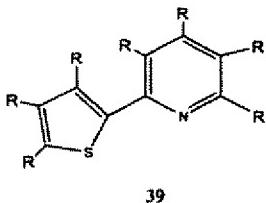
14. The use as claimed in any of claims 1 to 13, characterised in that at least one ligand is one of the following compounds 20-26, 29-37, where R,



is, in each case and independently of one another, any substituent, including hydrogen, E is an atom selected from the group C, Si, Ge, Sn, Pb, and in each case P, As or Sb may be present, independently of one another, instead of N, and Se or Te may be present, in each case

independently of one another, instead of S.

15. The use as claimed in any of claims 1 to 14, characterised in that at least one ligand is one of  
5 the following compounds 39-44, 47-56

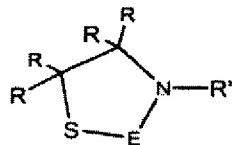


where R is, in each case and independently of one another, any substituent, including hydrogen, and R and R' can be

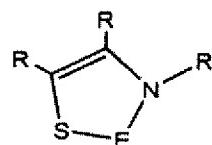
the same or different, E is an atom selected from the group of C, Si, Ge, Sn, Pb, and X is a heteroatom or carbon atom capable of acting as a donor, and in each case independently of one another P, As or Sb may be present instead of N, and Se or Te may be present, in each case independently of one another, instead of S.

16. The use as claimed in either of claims 14 or 15, characterised in that E is selected from the group of C (carbene), Si (silylene), Ge (germylene).
17. The use as claimed in any of claims 1 to 16, characterised in that at least one ligand is one of the following compounds 59-64

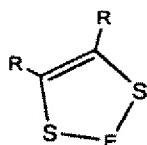
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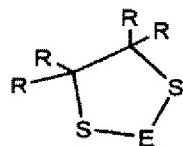
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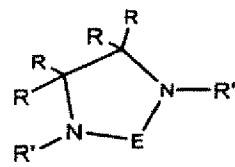
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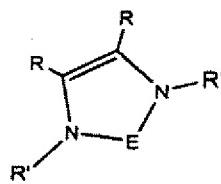
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where R is, in each case and independently of one another, any substituent, including hydrogen, E is an atom selected from the group of C, Si, Ge, Sn, Pb, and X is a heteroatom or carbon atom capable of acting as a donor, and in each case P, As or Sb may be present instead of N, independent-

ly of one another in each case, and Se or Te may be present instead of S, independently of one another in each case.

- 5 18. The use as claimed in any of claims 1 to 17, characterised in that at least one ligand is one of the above compounds 19, 38, 57 or 58, where R is, in each case and independently of one another, any substituent, including hydrogen, X is a heteroatom or carbon atom capable of acting as a donor, and in each case P, As or Sb may be used instead of N, independently of one another in each case.
- 10 19. The use as claimed in any of claims 1 to 18, characterised in that at least one, more or all of the rings carrying a donor atom have at least one or more substituted or unsubstituted alkyl substituents with C<sub>2</sub>-20.
- 15 20. The use as claimed in any of claims 1 to 19, characterised in that at least one ligand is a tripod ligand having the general structure:



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where R is any substituent, including H, where R can be identical to the structural sequence -X-Y, X represents an at least divalent atom or a group of atoms with or without heteroatoms, where X can be the same or different in each case, Y is a heteroatom or carbon atom capable of acting as a donor, where Y can be the same or different and can be part of a ring, and where Z, as the central atom of the

tripod ligand, is any atom, including a metal atom.

21. The use as claimed in claim 20, characterised in that Y is an atom from the group C, N, P, S, Se, Ge, Sn.

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22. The use as claimed in any of claims 1 to 21, characterised in that the complex is:  $M_2hpp_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(AlkylCOO)_4$  F with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W and with alkyl in each case, the same as each other or different from one another, with Cl to C10;  $M_2(guanidinate)_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(formamidinate)_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(carboxylate)_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W;  $M_2(halide)_4$  with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; bis( $\eta^5$ -cyclopentadienyl)M with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; benzene-M-( $\eta^5$ -cyclopentadienyl) with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; where optionally one or more of the hydrogen atoms of the ligands can be replaced by other residues, including alkyl residues.

23. The use as claimed in any of claims 1 to 22, characterised in that the metal complex has an ionisation potential in the gas phase of less than 6 eV or that the metal complex has an oxidation potential  $E(1/2)_{ox}$  against ferrocene/ferrocenium (Fe/Fe+) of  $\leq -0.09$  V.

24. A semiconducting material produced using a metal complex in accordance with any of claims 1 to 23 in the form of an electrically contactable layer or an electrical line path arranged on a substrate.

25. An organic semiconducting material containing at least one organic matrix compound and an n-dopant, character-

ised in that one or more neutral metal complexes in accordance with any of claims 1 to 23 is used as an n-dopant.

5 26. The organic semiconducting material as claimed in claim 25, characterised in that the molar doping ratio of dopant to matrix molecule or the doping ratio of dopant to monomeric units of a polymeric matrix molecule is between 1:1 and 1:100,000.

10 27. A process for producing an organic semiconducting material containing an organic matrix molecule and an n-dopant, characterised in that at least one or more neutral metal complexes in accordance with any of claims 1 to 23 is used as an n-dopant.

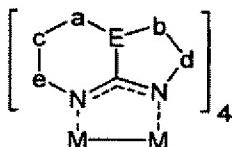
15 28. An electronic device with an electronically functionally effective region, characterised in that the electronically effective region is produced using at least one or more of the neutral metal complexes in accordance with any of claims 1 to 23.

20 29. The electronic device as claimed in claim 28, characterised in that the electronically effective region has an organic semiconducting matrix material which is doped with at least one n-dopant in order to alter the electronic characteristics of the semiconducting matrix material using at least one or more of the neutral metal complexes in accordance with any of claims 1 to 23.

30 30. The electronic device as claimed in either of claims 29 or 30 in the form of an organic light-emitting diode (OLED), a photovoltaic cell, an organic solar cell, an organic diode or an organic field effect transistor, in which the semiconducting organic material doped with at least one or more neutral metal complexes in accordance with any of

claims 1 to 23 represents an electronically effective part of the electronic device.

31. A dopant for doping an organic semiconducting matrix material, which has a structure selected from the group of:



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Type 65a

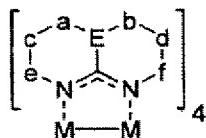
where

- the structural elements a-e may mean: a = -CR<sub>1</sub>R<sub>2</sub>-, b = -CR<sub>3</sub>R<sub>4</sub>-, c = -CR<sub>5</sub>R<sub>6</sub>-, d = -CR<sub>7</sub>R<sub>8</sub>- and e = -CR<sub>9</sub>R<sub>10</sub>-, where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> are, at the same time or independently of one another, H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, preferably R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, or
- optionally, a or b or e or d may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, or
- at c, C is replaced by Si,
- wherein the bonds b-d and c-e or b-d and a-c can, at the same time or independently of one another, be unsaturated,
- wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another, be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another be part of an aro-

matic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,

- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 10 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N, ,
- wherein the metal M is a transition metal, preferably W or Mo;

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Type 65b

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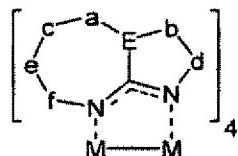
where

- the structural elements a-f may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$ , e =  $-CR_9R_{10}-$  and f =  $CR_{11}R_{12}$ , where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, - NR<sub>2</sub> or - OR, preferably R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, - NR<sub>2</sub> or - OR, the structure 65b with R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> = H being excluded from this, or
- in the structural elements c and/or d, C may be replaced by Si, or

30

- optionally, a or b or e or f may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or
- optionally, a and f or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl,
- wherein the bonds a-c, b-d, c-e and d-f, but not simultaneously a-c and c-e and not simultaneously b-d and d-f may be unsaturated,
- 10 - wherein the bonds a-c, b-d, c-e and d-f can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, b-d, c-e and d-f may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- 15 - wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 20 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;

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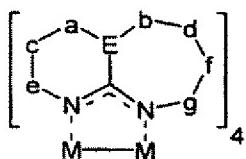
## Type 65c

where

- 5 - the structural elements a-f may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$ , e =  $-CR_9R_{10}-$  and f =  $CR_{11}R_{12}$ , where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> can, at the same time or independently from one another, be H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, - NR<sub>2</sub> or - OR, preferably R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, - NR<sub>2</sub> or - OR, or
- 10 - at c or e, C may be replaced by Si, or
- 15 - optionally, a or b or d or f may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, or
- 20 - optionally, a and d or b and f may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl,
- 25 - wherein the bonds a-c, c-e, e-f and b-d, but not simultaneously a-c, c-e and e-f and not simultaneously a-c and c-e and not simultaneously c-e and e-f may be unsaturated,
- 30 - wherein the bonds a-c, c-e, e-f and b-d can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, e-f and b-d may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,

- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 5 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or

10



15

Type 65d

- wherein the structural elements a-g may mean: a = -CR<sub>1</sub>R<sub>2</sub>-, b = -CR<sub>3</sub>R<sub>4</sub>-, c = -CR<sub>5</sub>R<sub>6</sub>-, d = -CR<sub>7</sub>R<sub>8</sub>-, e = -CR<sub>9</sub>R<sub>10</sub>-, f = CR<sub>11</sub>R<sub>12</sub> and g = CR<sub>13</sub>R<sub>14</sub>, where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub> can, at the same time or independently from one another, be H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, preferably, R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub>, R<sub>13</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub>, R<sub>14</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, or
- 20 - at c, d and f, though not d and f simultaneously, C may be replaced by Si, or
- 25 - at c, d and f, though not d and f simultaneously, C may be replaced by Si, or
- optionally, a or b or e or g may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, or

- optionally, a and g or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl,
- wherein the bonds a-c, c-e, b-d, d-f and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f and f-g, and not simultaneously b-d and d-f, and not simultaneously d-f and f-g, may be unsaturated,
- wherein the bonds a-c, c-e, b-d, d-f and f-g can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, b-d, d-f and f-g may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N
- wherein the metal M is a transition metal, preferably W or Mo.

32. A process for preparing a dopant in accordance with claim 31, comprising the steps of:

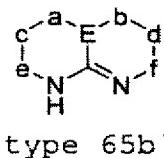
- (a) reacting an inorganic metal salt of the central atom M with a free base of a ligand defined in claim 38 in an organic solvent in the presence of a reducing agent and heating to reflux,

- (b) isolating the dopant product obtained after reacting and drying.
33. The process as claimed in claim 32, characterised in that  
5 the solvent is ether, an aromatic solvent or a mixture thereof.
34. The process as claimed in claim 33, characterised in that  
10 the ether is dialkyl ether, cyclic ether, cyclic and/or open-chain polyether.
35. The process as claimed in any of claims 32 to 34, characterised in that the reducing agent is a base metal.
- 15 36. The process as claimed in claim 35, characterised in that the base metal is sodium, potassium and/or caesium.
37. The process as claimed in any of claims 32 to 36, characterised in that the isolation is performed by crystallisation, precipitation and/or sublimation.  
20
38. A ligand for a metal complex, selected from the group consisting of
- 25
- Type 65a
- where
- the structural elements a-e may mean: a = -CR<sub>1</sub>R<sub>2</sub>-, b = -CR<sub>3</sub>R<sub>4</sub>-, c = -CR<sub>5</sub>R<sub>6</sub>-, d = -CR<sub>7</sub>R<sub>8</sub>- and e = -CR<sub>9</sub>R<sub>10</sub>-, where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> are, at the same time or independently of one another, H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkinyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, preferably R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cyclo-

alkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, where the structure 65a' with R<sub>1</sub> to R<sub>10</sub> = H is excluded from this, where the structure 65a' with R<sub>1</sub> and R<sub>2</sub> = aryl is excluded from this, where in the structure 65a' R<sub>1</sub> and R<sub>10</sub> are always H, or

- 5      - optionally, a or b or e or d may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or
- 10     - optionally a and d or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or
- 15     - at c, C is replaced by Si,
- 20     - wherein the bonds b-d and c-e or b-d and a-c can, at the same time or independently of one another, be unsaturated, wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another, be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, where the ligand with c-e = cyclohexyl and cyclohexenyl is excluded from this, or
- 25     - wherein the bonds b-d, a-c and c-e can, at the same time or independently of one another be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N, where the ligand in which b-d, a-c and c-e are components of benzene is excluded from this,
- 30     - wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

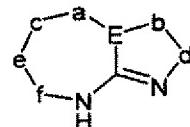
- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
  - wherein the metal M is a transition metal, preferably W or Mo;
- 5



where

- 10        - the structural elements a-f may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$ , e =  $-CR_9R_{10}-$  and f =  $CR_{11}R_{12}$ , where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are hydrogen,  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl,  $-NR_2$  or  $-OR$ , preferably  $R_1$ ,  $R_3$ ,  $R_5$ ,  $R_7$ ,  $R_9$ ,  $R_{11}$  = H and  $R_2$ ,  $R_4$ ,  $R_6$ ,  $R_8$ ,  $R_{10}$ ,  $R_{12}$  =  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl,  $-NR_2$  or  $-OR$ , the structure 65b with  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  = H being excluded from this, the ligand with  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , and  $R_{12}$  = phenyl, methyl, allyl,  $RSCH_2-$  and  $ROCH_2-$  being excluded from this, the ligand with  $R_9$  = phenyl,  $R_{10}$  = H,  $R_{11}$  = phenyl,  $R_{12}$  = H being excluded from this, the ligand with  $R_1$  = phenyl being excluded from this, the ligand with  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$  = phenoxy being excluded from this, or
- 15        - in the structural elements c and/or d, C may be replaced by Si, or
- 20        - optionally, a or b or e or f may be  $NR$  with R =  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl, or
- 25        - optionally, a and f or b and e may be  $NR$  with R =  $C_1-C_{20}$  alkyl,  $C_1-C_{20}$  cycloalkyl,  $C_1-C_{20}$  alkenyl,  $C_1-C_{20}$  alkynyl, aryl, heteroaryl,
- 30

- wherein the bonds a-c, b-d, c-e and d-f, but not simultaneously a-c and c-e and not simultaneously b-d and d-f may be unsaturated,
- wherein the bonds a-c, b-d, c-e and d-f can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, b-d, c-e and d-f may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N, the ligand in which a-c, b-d, c-e and d-f are components of benzene being excluded from this,
- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, excluding from this the ligand with a-E-b = component of cyclopentyl and pyranyl with R<sub>9</sub> to R<sub>12</sub> = alkyl, or
- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;



type 65c'

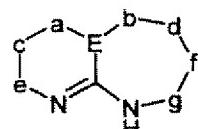
where

- the structural elements a-f may mean: a = -CR<sub>1</sub>R<sub>2</sub>-, b = -CR<sub>3</sub>R<sub>4</sub>-, c = -CR<sub>5</sub>R<sub>6</sub>-, d = -CR<sub>7</sub>R<sub>8</sub>-, e = -CR<sub>9</sub>R<sub>10</sub>- and f = CR<sub>11</sub>R<sub>12</sub>, where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> can, at the same time or independently from one

another, be H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, preferably R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, 5 C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, the ligand with R<sub>1</sub> to R<sub>12</sub> = H being excluded from this, or

- at c or e, C may be replaced by Si, or
- optionally, a or b or d or f may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or 10
- optionally, a and d or b and f may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl,
- wherein the bonds a-c, c-e, e-f and b-d, but not simultaneously a-c, c-e and e-f and not simultaneously a-c and c-e and not simultaneously c-e and e-f may be unsaturated, 15
- wherein the bonds a-c, c-e, e-f and b-d can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or 20
- the bonds a-c, c-e, e-f and b-d may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N, the ligand with E = N and simultaneously e-f and/or b-d as part of benzene or naphthalene being excluded from this, the ligand with E = N and simultaneously R<sub>7</sub> = R<sub>8</sub> = phenyl being excluded from this, the ligand with E = N and R<sub>3</sub> = phenyl, benzyl being excluded from this 25
- wherein the atom E is an element from the main group, preferably selected from the group N, P, As, Sb, though without being limited to these, the ligand with E=N and simultaneously the seven-membered ring with more than one unsaturated bond being excluded from this 30

- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 5 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or



10 Type 65d'

where

- the structural elements a-g may mean: a =  $-CR_1R_2-$ , b =  $-CR_3R_4-$ , c =  $-CR_5R_6-$ , d =  $-CR_7R_8-$ , e =  $-CR_9R_{10}-$ , f =  $CR_{11}R_{12}$  and g =  $CR_{13}R_{14}$ , where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  can, at the same time or independently from one another, be H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, preferably, R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>11</sub>, R<sub>13</sub> = H and R<sub>2</sub>, R<sub>4</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>10</sub>, R<sub>12</sub>, R<sub>14</sub> = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, -NR<sub>2</sub> or -OR, or
- at c, d and f, though not d and f simultaneously, C may be replaced by Si, or
- 15 - optionally, a or b or e or g may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl, or
- optionally, a and g or b and e may be NR with R = C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>20</sub> alkynyl, aryl, heteroaryl,
- 20 - wherein the bonds a-c, c-e, b-d, d-f and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f and f-g, and not simultaneously b-d and d-f, and
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 25 - the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or
- 30 - wherein the bonds a-c, c-e, b-d, d-f and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f and f-g, and not simultaneously b-d and d-f, and

not simultaneously d-f and f-g, may be unsaturated, the ligand in which b-d and f-g are simultaneously unsaturated being excluded from this,

- wherein the bonds a-c, c-e, b-d, d-f and f-g can be part of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, b-d, d-f and f-g may be part of an aromatic or condensed aromatic ring system which may also contain the heteroelements O, S, Se, N, the ligand in which c-e and f-g are simultaneously part of a benzene ring being excluded from this,
- wherein the atom E is an element from the main group, preferably selected from the group B, C, N, O, Si, P, S, As, Se, Sb, Te, particularly preferably selected from the group S, Se, N, P, though without being limited to these,
- wherein the structural element a-E-b may optionally be a component of a saturated or unsaturated ring system which may also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b may optionally be a component of an aromatic ring system which may also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo.

39. The use of a ligand in accordance with claim 38 in a process for preparing a dopant in accordance with any of claims 32-37.

Abstract

5 The invention relates to the use of a metal complex as an n-dopant for doping an organic semiconducting matrix material in order to alter the latter's electrical characteristics, the compound constituting an n-dopant with regard to the matrix material. In order to provide n-doped organic semiconductors  
10 even with matrix materials having a low reduction potential, while achieving high conductivities, it is proposed to use, as the dopant compound, a neutral electron-rich metal complex with a central atom as a preferably neutral or charged transition metal atom with a number of valence electrons of at least 16.  
15 The complex may in particular be polynuclear and possess at least one metal-metal bond. At least one ligand may form a n complex with the central atom; it may be a bridge ligand, especially hpp, a borate, carborane or triazacycloalkane, or may contain at least one carbanion-carbon atom or a divalent atom  
20 selected from the group C (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention likewise relates to novel n-dopants and processes for producing them.

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# Exhibit 7



## Deutschland

Anmelden | Sprache wechseln Suchen +

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Kontrollnummer

1ZER93996892813079

Anmelden für zusätzliche Informationen zur Sendungsverfolgung.

Andere Optionen der Sendungsverfolgung



## Statusabfrageergebnis - Detaillierte Informationen

Drucken Hilfe A A A

1ZER93996892813079

Aktualisiert: 04.04.2011 6:59 EST

Zugestellt

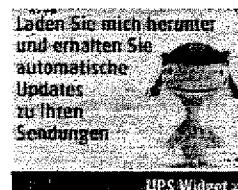
## Versandinformationen

An: GREIFSWALD, DE

Zugestellt am: Unterschrieben von:  
Montag, 04.04.2011 at 10:07 GROTHBenachrichtigung  
empfohlenHinterlegt bei: Zustellnachweis  
Büro

Versendet durch

UPS Standard®



## Weitere Informationen

Gewicht:  
0.50 kgTyp:  
PaketVersand bzw. in Rechnung gestellt am:  
01.04.2011

## Sendungsstatus

| Ort                     | Datum      | Ortszeit | Aktivität                           | Was ist das? |
|-------------------------|------------|----------|-------------------------------------|--------------|
| Neubrandenburg, Germany | 04.04.2011 | 10:07    | Zugestellt                          |              |
| Germany                 | 01.04.2011 | 9:13     | Auftrag verarbeitet: Für UPS bereit |              |

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| Result of status query - Detailed information     |                 |                     |                                | Print                                                         | Help | A A A |  |  |  |
|---------------------------------------------------|-----------------|---------------------|--------------------------------|---------------------------------------------------------------|------|-------|--|--|--|
| 1ZER93996892813079.                               |                 |                     |                                | Updated: 4th April, 2011 6:59 EST                             |      |       |  |  |  |
| <b>Delivered</b>                                  |                 |                     |                                | <b>Shipping information</b>                                   |      |       |  |  |  |
| Delivered on:<br>Monday, 4th April, 2011 at 10:07 |                 | Signed by:<br>GROTH | Add notification               | To: GREIFSWALD, DE<br><br>Shipped by:<br><u>UPS Standard®</u> |      |       |  |  |  |
| Left with:<br>Office                              |                 | Proof of delivery   |                                |                                                               |      |       |  |  |  |
| <b>Additional information</b>                     |                 |                     |                                |                                                               |      |       |  |  |  |
| <b>Weight:</b><br>0.50 kg                         |                 |                     |                                |                                                               |      |       |  |  |  |
| <b>Type:</b><br>Parcel                            |                 |                     |                                |                                                               |      |       |  |  |  |
| <b>Shipped or invoiced on:</b><br>1st April, 2011 |                 |                     |                                |                                                               |      |       |  |  |  |
| <b>Delivery status</b>                            |                 |                     |                                |                                                               |      |       |  |  |  |
| Place                                             | Date            | Local time          | Activity                       | What is this?                                                 |      |       |  |  |  |
| Neubrandenburg, Germany                           | 4th April, 2011 | 10:07               | Delivered                      |                                                               |      |       |  |  |  |
| Germany                                           | 1st April, 2011 | 9:13                | Order processed: ready for UPS |                                                               |      |       |  |  |  |

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# Exhibit 8

Novaled AG • Tatzberg 49 • 01307 Dresden

Herr Dr. Olaf Kühl

Wollweberstr. 10

17489 Greifswald

Dresden, 24.05.2011

**Patentanmeldung US10/585215**

Sehr geehrter Herr Dr. Kühl,

Ich habe gerade mit Ihrer Frau am Telefon gesprochen und vereinbart, dass ich Ihnen beiliegende Dokumente an Ihre Privatadresse zusende. Es handelt sich hierbei um die „Declaration for Patent Application US10/585215“ und das zugehörige „Assignment“ welche an das US-Patentamt bei einer Patentanmeldung übermittelt werden. In der Erklärung bestätigen Sie, dass Sie Miterfinder an der Patentanmeldung US10/585215 – „Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same“ sind. Den Anmeldetext lege ich Ihnen in Form der vom US-Patentamt veröffentlichten Version bei.

Wir haben bereits mehrfach versucht Sie zu kontaktieren, aber leider keine Rückmeldung erhalten. Zwischenzeitlich sind Sie umgezogen, wie ich gesehen habe. Am 01.04. habe ich die Dokumente an die Uni Greifswald (Institut für Biochemie) zu Ihren Händen gesandt und darum gebeten, sie unterschrieben zurückzusenden, aber keine Antwort erhalten. Nun habe ich heute mit Frau Voss (Sekretariat, Mathematisch-Naturwissenschaftliche Fakultät, Universität Greifswald) am Telefon gesprochen und Sie teilte mir mit, dass Sie seit dem 01.04.2011 nicht mehr regelmäßig an der Uni sind. Nun war mir nicht klar, ob Sie die Dokumente erhalten haben? Daher hatte ich heute bei Ihnen zu Hause angerufen.

Ich habe auf der „Declaration“ Ihre Adresse aktualisiert und würde Sie darum bitten, diese Änderung zusätzlich an betreffender Stelle gegenzuzeichnen. Wir bedanken uns im Voraus.

Falls Sie weiterhin keine Unterschrift leisten werden, bitte ich Sie um eine kurze diesbezügliche Information (z.B. per email: [manuel.a.krumbiegel@novaled.com](mailto:manuel.a.krumbiegel@novaled.com)).

Bei Fragen erreichen Sie mich gern unter Tel. 0351-796 5852.

Ich wünsche Ihnen Frohe Ostern.

Mit freundlichen Grüßen



Manuela Krumbiegel  
IP Officer

Novaled AG • Tatzberg 49 • 01307 Dresden

Dr. Olaf Kühl  
Wohlweberstr. 10  
17489 Greifswald

Dresden, 24th May, 2011

**Patent application US10/585215**

Dear Dr. Kühl,

I have just spoken to your wife on the telephone, and we have arranged that I should send the enclosed documents to you at your home address. The documents are the enclosed "Declaration for Patent Application US10/585215" and the corresponding "Assignment", which are sent to the US Patent and Trade Mark Office when a patent application is filed. In the declaration, you confirm that you are a co-inventor of the patent application US10/585215 - "Use of a metal complex as an n-dopant for an organic semiconducting matrix material, organic semiconducting material and electronic component, and also a dopant and ligand and process for producing same". I enclose the text of the application in the form of the version published by the US Patent and Trade Mark Office.

We have already tried a number of times to contact you, but unfortunately we have received no reply. I see you have moved in the meantime. On 1st April, I sent the documents to Greifswald University (Institute of Biochemistry) for your attention and asked for them to be signed and returned, but I received no reply. I have today spoken to Mrs. Voss (secretariat, Faculty of Mathematics and Science, Greifswald University) by telephone, and she informed me that you have no longer been at the University regularly since 1st April, 2011. It was then unclear to me whether you had received the documents. For this reason, I telephoned your home today.

I have updated your address on the "Declaration" and would therefore ask you also to countersign that alteration in the appropriate place. Many thanks in advance.

If you do not intend to provide a signature, might I ask you to inform me briefly to that effect (e.g. by e-mail: [manuela.krumbiegel@novaled.com](mailto:manuela.krumbiegel@novaled.com)).

If you have any questions, you can reach me at Tel. 0351-7965852.

Have a Happy Easter.

Yours faithfully,

Manuela Krumbiegel  
IP Officer

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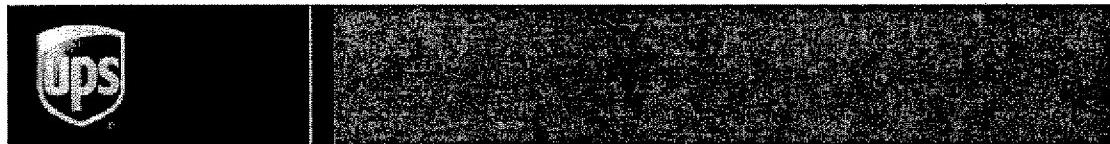
# **Exhibit 9**

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**Von:** shipping [shipping@noaled.com]  
**Gesendet:** Mittwoch, 27. April 2011 08:01  
**An:** manuela.krumbiegel@noaled.com  
**Betreff:** WG: UPS - Fehlerbenachrichtigung, Kontrollnummer 1ZER93996890893504  
Hallo Manu,  
der Empfänger hat die Annahme verweigert, die Sendung kommt nun zu uns zurück.  
Gruß Diana

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**Von:** UPS Quantum View [mailto:auto-notify@ups.com]  
**Gesendet:** Dienstag, 26. April 2011 20:02  
**An:** shipping@noaled.com  
**Betreff:** UPS - Fehlerbenachrichtigung, Kontrollnummer 1ZER93996890893504



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**Behebung der Ausnahme:** RETURNED TO SHIPPER (RESOLUTION)  
**Rücksendung an:**  
Diana Metzner  
Novaled AG  
Tatzberg 49  
Dresden  
01307  
DE

### Sendungsdetails

**Empfänger:**  
Dr. Olaf Kuehl  
Wollweberstr. 10  
GREIFSWALD  
17489  
DE  
**UPS Service:** STANDARD

**Grund der Verzögerung:** THE RECEIVER DID NOT WANT THE ORDER AND REFUSED THIS DELIVERY

**Behebung der Ausnahme:** RETURNED TO SHIPPER (RESOLUTION)

**Rücksendung an:**

Diana Metzner  
Novaled AG  
Tatzberg 49  
Dresden  
01307  
DE

### Sendungsdetails

**Empfänger:**

Dr. Olaf Kuehl  
Wollweberstr. 10  
GREIFSWALD  
17489  
DE

**UPS Service:** STANDARD

**Gewicht:** 0,2 KGS

**Referenznummer 1:** Manuela Krumbiegel

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**Exception Reason:** THE RECEIVER DID NOT WANT THE ORDER AND REFUSED THIS DELIVERY

**Exception Resolution:** RETURNED TO SHIPPER (RESOLUTION)

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Dresden  
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**Shipment Detail**

**Ship To:**

Dr. Olaf Kuehl  
Wollweberstr. 10  
GREIFSWALD  
17489

DE

**UPS Service:** STANDARD

**Weight:** 0,2 KGS

**Reference Number 1:** Manuela Krumbiegel

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# Exhibit 10

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Betreff: [Fwd: Nov22-US Olaf Kühl related]  
Von: Volker Scholz <V.Scholz@boehmert.de>  
Datum: Thu, 09 Jun 2011 08:16:12 +0200

-----  
\*Von:\* Manuela Krumbiegel  
\*Gesendet:\* Montag, 2. Mai 2011 08:57  
\*An:\* oevel@yahoo.com  
\*Cc:\* olaf.kuhl@gmail.com  
\*Betreff:\* Assignment and Power of Attorney for Patent application  
US10/585215

Guten Morgen Herr Dr. Kühl,

ich hatte Ihnen vor einer Woche Dokumente zur Unterschrift zugesandt, welche ich mit dem Vermerk zurück erhalten habe, dass Sie die Unterlagen nicht annehmen.

Gehe ich richtig in der Annahme, dass Sie die Unterschrift nicht leisten wollen? Oder liegt hier ein Missverständnis vor? In letzterem Fall würde ich Ihnen die Unterlagen gern noch einmal zusenden.

Über eine kurze Nachricht Ihrerseits wäre ich sehr dankbar.

Mit freundlichen Grüßen

Manuela Krumbiegel  
IP Officer

NOVALED AG  
Tatzberg 49  
01307 Dresden  
Germany

phone +49-351-796-5852 (-580)  
fax +49-351-796-5829  
web <http://www.novaled.com>

Novaled Aktiengesellschaft, Registered Office: 01307 Dresden, Companies Register: Amtsgericht Dresden, HRB 24467, Board of Directors: Gildas Sorin, Harry B?me, Gerd G?ther; Chairman of the Supervisory Board: Thilo von Selchow

-----  
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(Translation)

**From:** Manuela Krumbiegel  
**Sent:** Monday, 2nd May, 2011 8:57 a.m.  
**To:** oevel@yahoo.com  
**Cc:** olaf.kuhl@gmail.com  
**Re:** Assignment and Power of Attorney for Patent application US10/585215

Good Morning Dr. Kühl,

A week ago, I sent you some documents for documents for signing, which were returned to me with a notice that you do not accept the documents.

Am I right in assuming that you are unwilling to sign? Or has there been a misunderstanding? In the latter case, I should be happy to send you the documents again.

I should be very grateful for a short message from you.

Yours faithfully,

Manuela Krumbiegel  
IP Officer

NOVALED AG  
Tatzberg 49  
01307 Dresden  
Germany